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MOLYBDENUM IN ENAMELS: I, ADHERENCE PRODUCED WITH MOLYBDENUM COMPOUNDS*

By Karl Kautz

Abstract

When definite types of white or clear enamel are milled with certain molybdenum compounds, light-colored ground coats are produced. These ground coats show excellent adherence when applied in the usual manner to deeply pickled sheet steel. Firing may be done at 1600°F. or at 1500°F., according to the type of enamel. The paper also discusses the properties of molybdenum compounds, the problems involved in their use, the types of compounds which produce adherence, the type of enamels which work successfully, and a possible explanation of how these compounds function to produce adherence.

I. Introduction

Molybdenum compounds are used today in limited quantities in the ceramic industry. Very little is known about their ceramic behavior and only a few published articles mentioning molybdenum have been found.

Housley and King[1] smelted 7.5% of antimony trioxide and 1.5% of molybdenum trioxide in a typical colorless enamel base and obtained evidence of enamel adherence to sheet steel.

Amberg, Prior, and Richmond[2] found that a deposit of a hydrated suboxide of molybdenum formed by electrodeposition on the surface of sheet steel caused a white enamel to adhere tenaciously.

The experiment of Housley and King seemed to offer commercial possibilities for producing light-colored ground coats. A thorough check of this enamel in the laboratory and in the plant, however, failed to show satisfactory adherence to sheet steel. Changing the enamel formula and smelting in various amounts of Sb_2O_3 and MoO_3 still failed to produce satisfactory enamel adherence. Chemical analyses showed that when MoO_3 was smelted in an enamel only a portion remained because MoO_3 is readily volatile at smelting temperatures. The MoO_3 remaining did not function as an adherence-promoting agent.

A clear frit was milled with 3% of Sb_2O_3 and 1.5% of MoO_3. This enamel gave excellent adherence to sheet steel when it was applied in the usual manner; severe tearing or crawling resulted when it was fired. It showed, however, that MoO_3 in conjunction with Sb_2O_3 could be used to promote adherence of ground coats to steel.

II. Properties of Molybdenum and Some of Its Compounds

(1) Molybdenum

Molybdenum is a hard, silver-white metal. It is oxidized easily to MoO_3 in air at elevated temperatures. Its melting point is extremely high (4748°F.), and it makes excellent electrical resistors for high-temperature work when it is protected from oxidation. Its principal use as a metal is in filaments, screens, and grids for radio tubes.

(2) Molybdenum Trioxide

Molybdenum trioxide (MoO_3) is the stable, high-temperature oxide. It is formed when molybdenite (MoS_2), metallic molybdenum, and other compounds are heated in excess air. When it is pure, it forms yellowish white rhombic crystals with a melting point of 1463°F. Its vapor pressure is slight at 1100°F.; at 1300°F., it is 0.30 mm. of Hg; at the melting point, it is 10 mm. of Hg; and at 2111°F., it is 760 mm. of Hg. It thus sublimes to some extent even before it melts. The trioxide is a good oxidizing agent, readily furnishing oxygen in the presence of oxidizable substances, both in wet and thermal reactions. Like SO_3, it unites directly with alkalis, alkaline earths, and other metallic oxides to form molybdates. It is one of those chemical compounds which form a great number of complex compounds with other elements and compounds.

Molybdenum trioxide is soluble in water. At room temperature, 0.1 gram will dissolve in 100 cc. of water and 2.0 grams in the same quantity of boiling water.

(3) Molybdenum Dioxide

When molybdenum trioxide (MoO_3) is heated in a current of a reducing gas or in contact with a solid reducing agent at about 1400°F., it is reduced to brown molybdenum dioxide. Purple or violet-colored oxides are formed at lower temperatures. Analyses indicate that these oxides are probably $MoO_2 \cdot 2MoO_3$ or Mo_3O_8.

Molybdenum dioxide is insoluble in water, it has a high melting point, and it is oxidized readily to MoO_3 when it is heated in air (even below a red heat).

(4) Molybdates

Molybdite (MoO_3) is acidic in character. It combines directly with most bases or basic oxides either by wet or thermal reactions. It does not combine directly with SiO_2, but it forms complex, hydrated molybdosilicates. Like the analogous sulfates, the most common insoluble molybdates are lead and barium. Calcium molybdate is only slightly soluble in water. The

* Presented at the Forty-Second Annual Meeting, The American Ceramic Society, Toronto, Canada, April 10, 1940 (Enamel Division). Received April 10, 1940.

[1] W. L. Housley and R. M. King, "Mechanics of Enamel Adherence: XI, Application of Theory of Dendritic Adherence to Development of White Ground Coats for Sheet Steel," *Jour. Amer. Ceram. Soc.*, **18** [10] 319–20 (1935).

[2] C. R. Amberg, H. D. Prior, and J. C. Richmond, "Adhesion of Enamel to Steel Produced by Electrodeposition of $Mo(OH)_3$ on Steel," *ibid.*, **20** [3] 75–76 (1937).

normal molybdates of the alkalis, alkaline earths, lead, and zinc have high melting points and are all white compounds.

III. Problems Involved in Use of Molybdenum Compounds in Enamels

As mentioned previously, MoO_3 does not function as an adherence-promoting agent when it is smelted in an enamel. When it is milled into the frit along with Sb_2O_3, it functions to promote adherence. Because MoO_3 is soluble in the mill liquor, however, it causes the enamel coat to crack during drying, which results in crawling or tearing during firing. Molybdenum trioxide unites with water to form the compound, molybdic acid (H_2MoO_4), which shrinks when it is dehydrated. This shrinkage of molybdic acid in an applied enamel coat causes cracks to form in the drying coat, which is often accompanied by peeling.

Soluble compounds, such as sodium molybdate, moreover cannot be used in milled enamels because they cause scumming and tearing of the enamel coat.

The problem thus became one of finding an insoluble form of molybdenum which would still function as an adherence-promoting agent in fired ground coats. Many different kinds of compounds, both simple and complex, were made and tried experimentally in clear ground coats. The compounds, or mixtures, described in the following sections are the best developed up to the present time, but they may not be the best ultimately possible.

IV. Molybdenum Compounds Which Promote Adherence as Mili Additions

(1) Molybdenum Trioxide

A mixture of Sb_2O_3 and MoO_3 milled into a clear enamel base produced excellent adherence within certain limits. A study was made varying the amount of Sb_2O_3 from 0 to 4% and of MoO_3 from 0 to 4%. Poor adherence was obtained when 3% and 4% of MoO_3 was used regardless of the Sb_2O_3 content. Zero content of MoO_3 with 1 to 4% of Sb_2O_3 gave only weak adherence, and zero content of Sb_2O_3 with 1 to 4% of MoO_3 gave poor adherence. The best adherence was obtained when 1% and 2% of MoO_3 was used, with the Sb_2O_3 ranging from 1 to 4%, and it always seemed to be associated with a ratio of 2 parts by weight of Sb_2O_3 to one part by weight of MoO_3. This led to the belief that the molecular proportion of Sb_2O_3 to MoO_3 (292 : 144) might possibly produce the best adherence. If this assumption is true, the compound $Sb_2O_3 \cdot MoO_3$ should promote excellent adherence, and experiments with this compound (to be described) confirmed the theory.

(2) Antimonyl Molybdate

Antimonyl molybdate ($Sb_2O_3 \cdot MoO_3$), which may also be written as $(SbO)_2MoO_4$, was made by heating an intimate mixture of Sb_2O_3 and MoO_3 in molecular proportions to 1500°F. in the absence of air. The melting point of this compound is approximately 890°F. It forms a yellow-brown crystalline mass when it is cooled, which becomes brownish yellow or ochre-colored with fine grinding. Additions of 3 or 4% of this compound produced excellent adherence when they were milled with a clear enamel base. The two most serious objections to its use are the brownish yellow color imparted to the enamel and a slight tendency to crawl.

(3) Barium Antimony Molybdates

To render the antimony and molybdenum oxides even more insoluble, barium oxide was introduced in molecular ratios of (*a*) $2BaO \cdot Sb_2O_3 \cdot MoO_3$, (*b*) $BaO \cdot Sb_2O_3 \cdot MoO_3$, and (*c*) $BaO \cdot Sb_2O_3 \cdot 2MoO_3$.

The first calcine, which possibly may be the double compound, $Ba(SbO_3) \cdot BaMoO_4$, is pure white. This compound, or calcine, gives excellent adherence as well as good opacity when it is milled into a clear enamel base. Further experimental work, however, is necessary to make this compound commercially successful because of the erratic behavior of some of the batches. Some calcines worked splendidly, whereas others failed. This calcine must be controlled within a narrow range of time, temperature, and degree of oxidation to produce the desired results.

The second calcine, $BaO \cdot Sb_2O_3 \cdot MoO_3$, is brownish yellow, and it is produced only when it is calcined in the absence of air. It imparts a slight yellowish color to the enamel, and it causes slight tearing.

The third calcine, $BaO \cdot Sb_2O_3 \cdot 2MoO_3$, is light brown, and it is produced by calcining in the absence of air. It imparts a yellow-brown color to the enamel, and it causes severe crawling.

(4) Calcium Antimony Molybdate

Calcium antimony molybdate ($2CaO \cdot Sb_2O_3 \cdot MoO_3$), corresponding to the barium compound, was prepared by calcining the proper molecular proportions. This calcine, which is yellow-brown, produces poor adherence and severe crawling.

(5) Compound Molybdates

The compounds, calcium molybdate ($CaO \cdot MoO_3$), barium molybdate ($BaO \cdot MoO_3$), lead molybdate ($PbO \cdot MoO_3$), stannous molybdate ($SnO \cdot MoO_3$), and ferrous molybdate ($FeO \cdot MoO_3$), did not work successfully when they were used alone. With the addition of Sb_2O_3 or with the antimonates of calcium or barium, fair adherence was obtained with some of these molybdates.

(6) Molybdenum Blue

Molybdenum blue is the name given to the suboxides obtained by reducing MoO_3 when it is suspended in water. The composition is variable and may be represented by the formula, $xMoO_2 \cdot yMoO_3 \cdot zH_2O$. It forms deep-blue colloidal suspensions in water with properties similar to a dyestuff. When it is milled with a clear frit and Sb_2O_3, it gives excellent adherence, but it tends to crawl severely.

(7) Molybdenum Dioxide

Molybdenum dioxide (MoO_2) is produced when MoO_3 is heated with a reducing agent, either solid or

gaseous. It produces excellent adherence when it is milled with Sb_2O_3 in a clear frit. Unlike MoO_3, it produces no crawling, tearing, or peeling in the enamel because it is insoluble in the mill liquor. Excellent working properties in the slip as well as excellent adherence on fired specimens result when MoO_2 is used in amounts of 0.5 to 2% and Sb_2O_3 in amounts of 0.5 to 3%. A proportion of 2.25% of Sb_2O_3 and 1.25% of MoO_2 was used successfully in many enamels. The theoretical proportions of 2.92% of Sb_2O_3 and of 1.28% of MoO_2 give excellent adherence, but they are sometimes accompanied by "antimony blisters," which are eliminated if an excess of MoO_2 is used. The proper amounts to use depend on the nature of the heat treatment.

FIG. 1.—Impact tests for adherence on specimens fired at 1600°F. This blended series shows the greatly increased adherence resulting when MoO_2 is added to an enamel containing 3% of Sb_2O_3 as a mill addition.

V. Successful Types of Enamels with Antimony-Molybdenum Oxide Combinations

The most successful enamel batches have been found to be almost identical with those developed for the cobalt enamels. A typical enamel of this type, smelted without the addition of cobalt, nickel, and manganese oxides, will produce excellent adherence when it is milled with Sb_2O_3 and MoO_2.

When Sb_2O_3 and MoO_2 are used as the adherence-promoting agents, an enamel with high zinc-oxide content generally produces poor adherence. Phosphorus pentoxide (P_2O_5), introduced as calcium phosphate or bone ash, and high fluorine, introduced as cryolite, cause blistering. Fluorine (not over 0.3 molecular equivalent) may be introduced as fluorite without difficulty.

Adherence is adversely affected by most opacifiers. When antimony oxide is smelted into the enamel batch, there is a decrease in adherence although possibly not enough to cause serious commercial difficulties. Milled-in opacifiers, such as the commercial zirconium opacifiers, also cause a slight decrease in adherence.

From the data to be presented, it may be seen that enamels of the proper composition may be compounded for any firing range between 1450° and 1600°F. and that good adherence may be obtained by milling Sb_2O_3 and MoO_2 in the proper amounts.

VI. Factors Affecting Adhesion of Vitreous Enamels to Sheet Steel

(1) Physical Condition of Metal Surface

The prime requisite for the adherence of any vitreous enamel is an iron surface, free from grease, oil, or dirt. The degree of pickling or etching of the surface depends on the oxidizing conditions encountered in the firing process. In laboratory furnaces with a slow comeback, deep etching is necessary to bring about maximum adherence. In industrial (box and continuous) furnaces, where severe oxidizing conditions and rapid heat transfer occur, lighter pickling is sufficient for good adherence.

(2) Enamel Composition and Fluidity

A successful ground coat must have good fluidity so that the gas generated by reactions occurring at the iron surface during the firing may escape without permitting excessive oxidation of the iron base. For this reason, great care must be exercised when heavy opacifiers are added to ground coats. The composition of the ground coat must be such that iron oxides are easily absorbed.

(3) Oxygen-Carrying Ability of Adherence-Promoting Agents

The third factor to influence the adhesion of enamels to iron is the presence of oxygen-carrying agents in the enamel. Cobalt and nickel are understood to function because they are able to absorb oxygen from the air and give it up to the iron base. Molybdenum oxides, in combination with antimony trioxide, are also understood to do this.

VII. Probable Explanation of Function of Antimony and Molybdenum Oxides in Enamels

It has been stated that MoO_3 smelted in enamels does not produce adherence. Because antimonyl molybdate ($Sb_2O_3 \cdot MoO_3$) as well as mixtures of Sb_2O_3 and MoO_3 and of Sb_2O_3 and MoO_2 functions as mill additions to produce adherence, the compound, $Sb_2O_3 \cdot MoO_3$, and not a glass solution of these compounds, is believed to be the oxygen carrier.

The compound, $Sb_2O_3 \cdot MoO_3$, forms readily when a mixture of Sb_2O_3 and MoO_3 is heated. It is a compound of low fusibility, and it easily corrodes or oxidizes iron. Antimony trioxide does not dissolve readily in enamels, but it combines with MoO_3 below the softening point of the frit. This is probably the reason that MoO_3 can function as an oxygen carrier only in the presence of Sb_2O_3.

When a light-colored ground coat, containing milled-in Sb_2O_3 and MoO_2, is heated in contact with iron, the following reactions might occur:

$$(1)\ 2Sb_2O_3 + 2MoO_2 + O_2 \longrightarrow 2Sb_2O_3 \cdot MoO_3$$
$$(2)\ Sb_2O_3 \cdot MoO_3 + Fe \longrightarrow FeO + Sb_2O_3 + MoO_3.$$

In the early stages of firing before the enamel fuses, MoO_2 absorbs oxygen to form MoO_3, which combines with Sb_2O_3 to form antimony molybdate ($Sb_2O_3 \cdot MoO_3$). This has a two-fold purpose, namely, (1) by rapidly absorbing atmospheric oxygen, excessive primary oxidation of the iron base may be prevented and (2) by forming the very fusible antimonyl molybdate, the unfused coating tends to become vitrified, thereby diminishing further primary oxidation of the iron base.

The iron base is oxidized by the liberation of some of the available oxygen in the antimony molybdate; the

latter is then regenerated by oxygen carried into the glass from the furnace atmosphere. This reaction is probably cyclical throughout the firing period. Oxidation of the iron base has been observed to take place continuously under the fused glassy coating because these enamels, with prolonged heat treatment, readily tend to become saturated with iron oxides, that is, they become black or "burned off."

VIII. Typical Enamels and Mill Batches

For ground coats maturing at 1580° to 1600°F., a number of compositions work successfully; in fact, almost any cobalt enamel batch without the coloring oxides may be used. A typical enamel in this range is as follows:

ENAMEL NO. 1

Empirical molecular formula

$$\left.\begin{matrix}0.15\ K_2O\\0.60\ Na_2O\\0.25\ CaO\end{matrix}\right\}0.15\ Al_2O_3\left\{\begin{matrix}2.00\ SiO_2\\0.60\ B_2O_3\\0.25\ F_2\end{matrix}\right.$$

Smelter batch	(%)
Borax	35.5
Feldspar	26.0
Quartz	20.5
Soda ash	6.6
Soda niter	5.3
Fluorite	6.1
	100.0

A *B* *C* *D*

FIG. 2.—Impact tests for adherence on specimens fired at 1600°F. (*A*) enamel No. 1, (*B*) enamel No. 1 plus a mill addition of 8% of ZrO_2, (*C*) enamel No. 2, (*D*) enamel No. 2 plus a mill addition of 8% of ZrO_2.

When enamel No. 1 is smelted with antimony oxide, the batch is as follows:

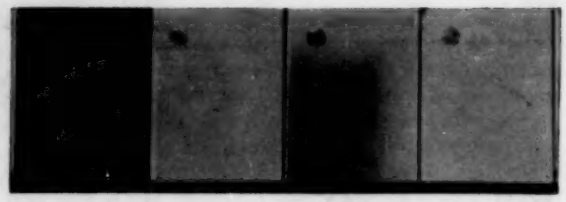
ENAMEL NO. 2

Empirical molecular formula

$$\left.\begin{matrix}0.15\ K_2O\\0.60\ Na_2O\\0.25\ CaO\end{matrix}\right\}0.15\ Al_2O_3\left\{\begin{matrix}2.00\ SiO_2\\0.60\ B_2O_3\\0.25\ F_2\\0.04\ Sb_2O_5\end{matrix}\right.$$

Smelter batch	(%)
Borax	34.40
Feldspar	25.00
Quartz	19.80
Soda ash	6.40
Soda niter	5.10
Fluorite	5.80
Antimony trioxide	3.50
	100.00

Enamel No. 3 is a soft ground coat that may be fired at 1500°F. or lower.



A *B* *C* *D*

FIG. 3.—Impact tests for adherence on specimens fired at 1500°F. (*A*) enamel No. 3, (*B*) enamel No. 3 plus 8% of ZrO_2, (*C*) enamel No. 4, (*D*) enamel No. 4 plus 8% of ZrO_2.

ENAMEL NO. 3

Empirical molecular formula

$$\left.\begin{matrix}0.10\ K_2O\\0.60\ Na_2O\\0.20\ CaO\\0.10\ BaO\end{matrix}\right\}0.10\ Al_2O_3\left\{\begin{matrix}1.50\ SiO_2\\0.80\ B_2O_3\\0.20\ F_2\end{matrix}\right.$$

Smelter batch	(%)
Borax	47.40
Feldspar	17.30
Quartz	16.80
Soda ash	4.90
Soda niter	2.70
Barium carbonate	6.10
Fluorite	4.80
	100.00

At 1500°F., or lower, a small amount of antimony trioxide is smelted to make up enamel No. 4.

ENAMEL NO. 4

Empirical molecular formula

$$\left.\begin{matrix}0.10\ K_2O\\0.60\ Na_2O\\0.20\ CaO\\0.10\ BaO\end{matrix}\right\}0.10\ Al_2O_3\left\{\begin{matrix}1.50\ SiO_2\\0.80\ B_2O_3\\0.20\ F_2\\0.04\ Sb_2O_5\end{matrix}\right.$$

Smelter batch	(%)
Borax	45.80
Feldspar	16.70
Quartz	16.20
Soda ash	4.70
Soda niter	2.50
Barium carbonate	5.90
Fluorite	4.70
Antimony trioxide	3.50
	100.00

These frits, milled in the usual manner to about 8 grams on 200-mesh for a 100-gram sample, give a typical mill batch as follows:

	Parts
Frit	1000
Vallendar clay	70
Borax	5
Water	550

The following amounts of adherence-promoting agents are added to the mill batch before milling:

	Parts
Sb_2O_3	22.5 (15–30)
MoO_3	12.5 (7.50–20)

There is quite a range in the amounts and proportions of Sb_2O_3 and MoO_2 that produce good adherence, depending on the nature of the iron surface, the thickness of the coating, and furnace conditions. The proper additions for any particular set of conditions must be determined experimentally. Although it is not necessary, the Sb_2O_3 and MoO_2 may be wet-milled together and then dried before adding to the mill batch. This appears to improve the gloss and texture of the enamel and to give greater uniformity. A mixture of 65 parts of Sb_2O_3 and 35 parts of MoO_2, prepared in this manner, gave good results when used in amounts of 3 to 4% of the frit weight.

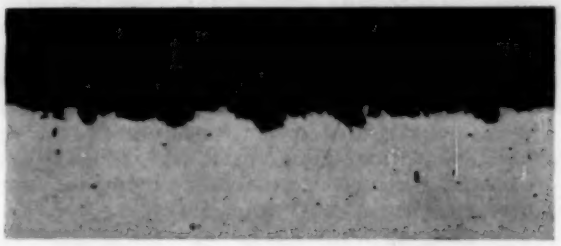


FIG. 4.—Section showing type of surface developed when enamel No. 1 is fired on sheet iron; 60×.

Antimonyl molybdate or barium antimony molybdate, prepared by methods already described, may be used in place of Sb_2O_3 and MoO_3. Suggested additions of these compounds are $Sb_2O_3 \cdot MoO_3$ 2.5 to 4.0% and $2BaO \cdot Sb_2O_5 \cdot MoO_3$ 5.0 to 8.0%.

IX. Discussion

The idea of adding the oxygen carriers or adherence-promoting agents as mill additions seems to be quite a departure from customary enameling practice. Numerous laboratory tests and several plant tests have demonstrated that the antimony-molybdenum combinations give adherence comparable with typical cobalt ground coats. Mill additions of adherence-promoting agents permit finer adjustments of the ground coat under operating conditions. Not only can two or more frits be blended at the mill but the proportions and amounts of Sb_2O_3 and MoO_2 may be varied. Certain opacifiers may also be added at the mill if it is desired, although the heavy opacifiers generally tend to decrease adherence. According to the tests conducted, zirconium opacifiers seem to give less trouble than tin oxide in this respect. Enamels containing high fluorine introduced as sodium fluoride may prove to be satisfactory.

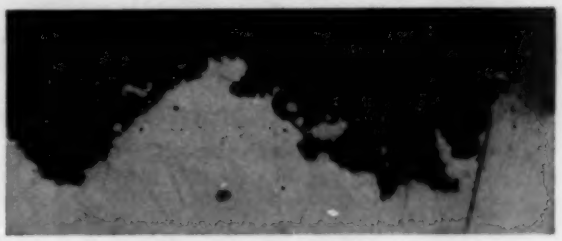


FIG. 5.—Same as Fig. 4, but at 350×.

The advantages of the molybdenum ground coat may be summarized as follows: (1) it lowers the cost, (2) it covers with less white enamel, (3) it reboils only slightly, (4) it makes low-temperature ground coats possible, and (5) it permits finer adjustment of the ground coat at the mill.

X. Summary

When molybdenum dioxide and antimony trioxide are milled into a clear enamel base, they produce adherence comparable to the typical cobalt ground-coat enamels. Soluble molybdenum trioxide plus Sb_2O_3 likewise produce adherence but cause drying difficulties. Other compounds, such as antimonyl molybdate or barium antimony molybdate, may also be used instead of Sb_2O_3 plus MoO_2. Enamels similar to those used with typical cobalt ground coats appear to give the best results, and the use of heavy opacifiers seems to cause a decrease in adherence.

A theory explaining the role of molybdenum dioxide and antimony trioxide as mill additions indicates what reactions may take place. Typical enamel batches and mill batches are given although these may be varied quite generally.

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SOLUBILITY OF A ZIRCONIUM OXIDE OPACIFIER IN ENAMEL GLASSES*

By A. I. Andrews and R. W. Gates

Abstract

The solubility of a zirconium oxide opacifier was determined by fusion in enamel glasses and then by heat-treating at enameling temperatures and noting the amount of crystallization. An increase in the alumina, zinc oxide, and calcium oxide content in the glasses caused a decided decrease in the solubility of the zirconium oxide opacifier. The fusion temperatures of the enamels were raised by solution of zirconium oxide.

I. Introduction

To obtain high reflectance in enamels, it is necessary that the opacifiers remain as small particles in an enamel glass. Because small particles present a large surface area for their mass, the solubility of the opacifying materials is an important consideration. In the present investigation, the relation between certain changes in the composition of the glass to the solubility of a zirconium oxide opacifier in the glass was studied.

The solution of zirconium oxide in the glass defeats the purpose for which it is added because part of the opacifier particles are eliminated and the solution of the zirconium oxide raises the index of refraction of the glass. Such an increase results in a smaller difference between the index of the glass and the opacifier particles, thereby decreasing the amount of reflectance.

Although at the present time most commercial ground coats are of the cobalt-blue type, a white ground coat has many advantages. Zirconium oxide is one of the few opacifiers that may be used to produce a white ground coat. Because opacity is due to insoluble particles of index of refraction different from the glassy phase, the main object of this investigation was to determine the effect of composition variation of a glass containing zinc oxide, alumina, and calcium oxide on the solubility of finely divided zirconium oxide particles.

II. Literature

There is only a limited amount of information available in the literature concerning the solubility of zirconium oxide in enamel glasses. Mernagh[1] states that the first 3 or 4% of zirconium oxide added to an enamel will be dissolved in the enamel and cause no opacity. Turner and his co-workers[2] introduced as much as 20% of zirconium oxide in fusions of soda-zirconia-silica glasses without obtaining opacity. The fact that the success or failure of zirconium oxide as an opacifying agent in enamels is related to the alumina content of the enamel was known to Grunwald[3] prior to 1914. According to Kinzie and Commons,[4] the explanation of the failure of zirconium oxide as an opacifier under certain conditions lies in the fact that the zirconium oxide goes into solution in certain types of compositions, thus eliminating the crystalline phase from the enamel glass. They also found that certain constituents, such as alumina, zinc oxide, calcium oxide, and barium oxide, are necessary or very beneficial in preventing the solution of zirconium oxide.

In a study by Dutton and Wagner,[5] a transparent enamel with 14% of zirconium oxide was made opaque by adding certain proportions of zinc oxide, calcium oxide, or barium oxide to the enamel.

The literature indicates that the solubility of zirconium oxide in glasses depends largely on the composition of the glass, but the investigations have not been extensive enough to answer many questions concerning the degree of solubility or the specific effects of different modifications of the glass composition.

III. Procedure

Because opacity due to high fluoride content was not the subject of this study, the amount of fluorspar in the base composition was kept low. This avoided the crystallization of fluorides, which would make it difficult to detect zirconium compounds that might form in the heat-treated sample. Color oxides were omitted from the base composition to give a transparent colorless glass. The composition of the raw batch used as a base enamel was as follows:

	Parts		Parts
Feldspar	30.0	Fluorspar	4.0
Borax	30.0	Zirconium oxide opacifier	Variables
Quartz	20.0	Zinc oxide	
Soda ash	8.0	Whiting	
Soda niter	3.0	Aluminum hydroxide	

The zirconium oxide opacifier used in this investigation had the following chemical composition:

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* Presented at the Forty-Second Annual Meeting, The American Ceramic Society, Toronto, Canada, April 10, 1940 (Enamel Division). Received April 29, 1940.

This paper is based on a thesis prepared by the junior author to satisfy in part the requirements for the degree of M.S. in Ceramics. It is published with the permission of the Dean of the Graduate School of the University of Illinois.

[1] L. R. Mernagh, Enamels: Manufacture and Application to Iron and Steel Ware, p. 96. Charles Griffin & Co., Ltd., London, 1928; *Ceram. Abs.*, **8** [2] 100 (1929).

[2] V. Dimbleby, S. English, E. M. Firth, F. W. Hodkin, and W. E. S. Turner, "Transparent Zirconia-Containing Glasses," *Jour. Soc. Glass Tech.*, **11** [41] 52–64 (1927); *Ceram. Abs.*, **6** [9] 376 (1927).

[3] Julius Grunwald, Raw Materials of Enamel Industry, p. 129. Charles Griffin & Co., Ltd., London, 1914.

[4] C. J. Kinzie and C. H. Commons, "Effect of Zirconium Oxide in Glasses, Glazes, and Enamels," *Jour. Amer. Ceram. Soc.*, **17** [10] 283–87 (1934).

[5] C. A. Dutton and B. F. Wagner, "Zirconium Oxide in Glasses and Enamels, II," *Ceram. Ind.*, **24** [2] 88 (1935); *Ceram. Abs.*, **14** [4] 88 (1935).

	(%)		(%)
ZrO_2	89.88	Al_2O_3 and P_2O_5	0.30
SiO_2	7.20	Na_2O	1.30
TiO_2	0.20	H_2O	0.08
FeO	0.10	Others	0.94

(1) Smelting and Heat Treatment

The raw batch was accurately weighed, thoroughly mixed, screened through a No. 60 screen, and then placed in a 9-inch fire-clay crucible, preheated to 2100° F. in a frit furnace. Each enamel was smelted at 2100° F. for one and one-half hours before being poured into two preheated 3-inch crucibles that were immediately placed in an electric furnace, held either at 1600° or 1900°F. After being heat-treated for eighteen hours, one sample was drawn out and examined to determine whether or not the enamel was transparent. The other sample remained in the furnace for fifty hours. At the end of the fifty-hour period, the second crucible was removed from the furnace and examined macroscopically, and while the enamel was still molten, a glass thread 0.5 mm. in diameter was drawn from the crucible for use in the fusion test, which is described later.

(2) Crystallization Point

The zirconium oxide saturation points of the enamel glasses were determined by smelting and heat-treating batches of the same enamel with varying amounts of zirconium oxide opacifier and then examining for crystals. If the enamel was a clear glass, another enamel with a larger amount of zirconium oxide opacifier was tried. Excessive amounts of zirconium oxide resulted in opaque enamels that contained many crystals. By this cut-and-try process, the solubility of the opacifiers in the different enamel compositions could be determined within 1%. It was also possible to detect by simple observation even the first trace of crystals in the molten glass as indicated by a check determination with the microscope. In no case did crystals form during the rapid cooling from the heat-treating temperature to room temperature.

(3) Fusion Tests

The threads prepared for the fusion tests were broken into $1^1/_2$-inch lengths and mounted at an angle of 82

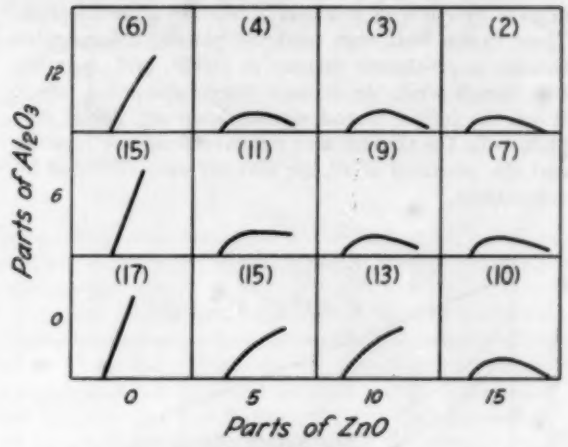

FIG. 1.—Positions of enamel threads saturated with zirconium oxide at 1600°F. with varying alumina and zinc oxide content after being heated to 1100°F. (zirconium oxide opacifier content shown in parentheses).

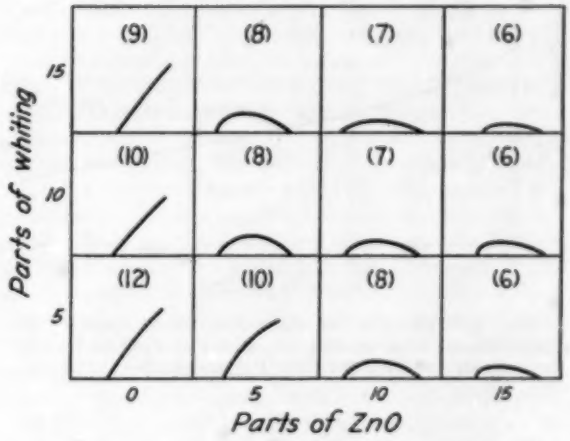

FIG. 2.—Positions of enamel threads saturated with zirconium oxide at 1600°F. with varying whiting and zinc oxide content after being heated to 1100°F. (zirconium oxide opacifier content of each enamel shown in parentheses).

TABLE I

ENAMEL COMPOSITIONS*

	Enamel No.†											
	1	2	3	4	5	6	7	8	9	10	11	12
Feldspar	30.0	30.0	30.0	30.0	30.0	30.0	30.0	30.0	0.0	0.0	0.0	0.0
Borax	30.0	30.0	30.0	30.0	30.0	30.0	30.0	30.0	30.0	30.0	30.0	30.0
Quartz	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	39.4	39.4	39.4	39.4
Soda ash	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	15.5	15.5	15.5	15.5
Soda niter	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Fluorspar	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Zirconium oxide	6.0	4.0	3.0	2.0	15.0	11.0	9.0	7.0	17.0	15.0	13.0	10.0
Aluminum hydroxide	9.1	9.1	9.1	9.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Zinc oxide	0.0	5.0	10.0	15.0	0.0	5.0	10.0	15.0	0.0	5.0	10.0	15.0

* All figures refer to parts by weight.

† Enamel compositions of samples Nos. 1 to 12 were heat-treated at 1600°F; base composition given in Section III contained 6 parts of alumina; alumina content was doubled in samples Nos. 1 to 4 by adding the calculated equivalent of aluminum hydroxide; samples Nos. 9 to 12 contained no alumina; to make a batch with no alumina, the feldspar was omitted, and the calculated equivalent of alkali and silica in the feldspar were added as soda ash and quartz.

degrees by inserting one end in holes in a porous plate. These fusion tests were made by placing the mounted threads in an electric furnace at 700°F. and observing the threads while the furnace temperature was raised. When the softest thread melted down at 1100°F., the plate with the threads was removed from the furnace, and the positions of all the threads were recorded for comparison.

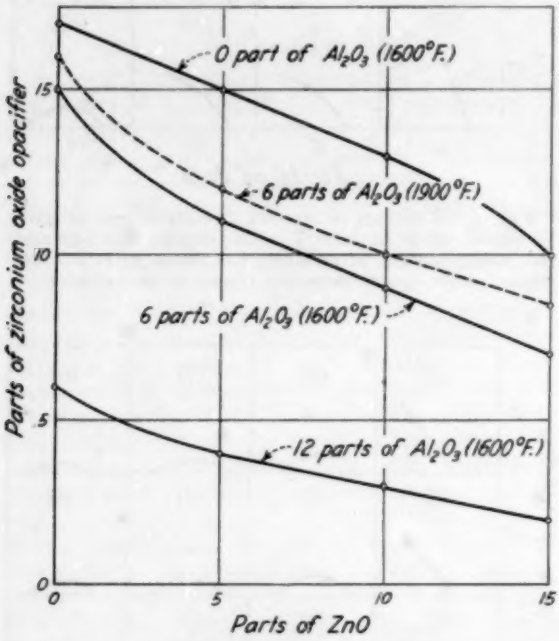

FIG. 3.—Solubility of zirconium oxide opacifier in base enamel with varying quantities of ZnO and Al_2O_3 heat-treated at 1600° or 1900°F. (samples No. 1 through No. 16).

IV. Data

From an examination of the position of the enamel threads that were heated to 1100°F. in the fusion test (Figs. 1 and 2), it is observed that the zirconium oxide opacifier that goes into solution causes the enamels to become more refractory. Although alumina and whiting are refractory ingredients of enamels, they do not increase the fusion temperatures as much as zirconium oxide. Because zinc oxide is a flux, it decreases the fusion temperature as it is added in increasing amounts.

The results given in Fig. 3 show that there is a gradual decrease in the solubility of zirconium oxide in the base enamel glass because the zinc oxide or alumina content, or both, is increased in the raw batch. Increases in the alumina content cause a greater decrease in the solubility of zirconium oxide than do equal increases in the zinc oxide content. With enamels high in alumina, small additions of alumina have a greater effect on the solubility of zirconium oxide in the enamel than do equal additions of alumina added to an enamel that has a low alumina content.

The quantity of zirconium-oxide opacifier required to saturate the enamel glass is increased about one part when the heat treatment is carried out at 1900°F. rather than at 1600°F.

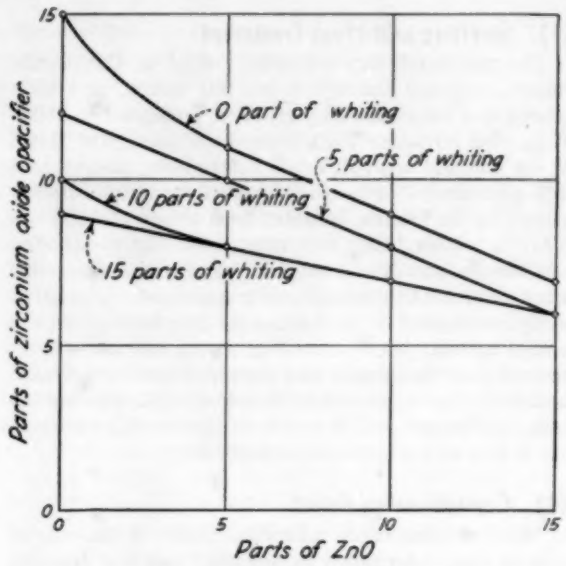

FIG. 4.—Solubility of zirconium oxide opacifier in base enamel with varying quantities of ZnO and whiting heat-treated at 1600°F. (samples No. 5 through No. 8 and No. 17 through No. 28).

With the alumina content constant, there is also a gradual decrease in the solubility of zirconium oxide with an increase of zinc oxide or whiting as shown by Figs. 3 and 4. Whiting, when added to an enamel to decrease the solution of zirconium oxide, does not continue to decrease solution appreciably after a certain quantity of whiting has been added.

V. Conclusions

Although the general conclusions from this study may deal broadly with any enamel, the data from which these conclusions were drawn deal with one base enamel in which the alumina, zinc oxide, whiting, and zirconium oxide opacifier content was varied.

The general conclusions drawn from this work are (1) as much as seventeen parts of zirconium oxide opacifier may be added without crystals forming in the heat treatment at 1600°F., but with large additions of alumina and zinc oxide, the same basic enamel will show crystals if more than two parts of zirconium oxide opacifier are present; (2) if the heat-treating temperature of the enamel is increased from 1600° to 1900°F., the results would indicate about one part more of opacifier in solution; (3) the ability of alumina, zinc oxide, and whiting to decrease the solution of zirconium oxide in enamel glass is in the order named; and (4) the refractoriness of the glass is increased as the quantity of zirconium oxide taken into solution is increased.

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DISCUSSION OF "RELATION OF DEFECTS IN ENAMEL COATINGS TO HYDROGEN IN STEEL" BY C. A. ZAPFFE AND C. E. SIMS

Editor's Note

This paper was published in *Jour. Amer. Ceram. Soc.*, 23 [7] 187–221 (1940). Following its presentation at the Forty-Second Annual Meeting, The American Ceramic Society, Toronto, Canada, April 9, 1940, before the Enamel Division, a two-hour discussion ensued. Those who participated have edited or extended their remarks that were recorded during the meeting.

W. H. PFEIFFER, CHAIRMAN: There are several prepared discussions by those who have had copies of the paper by C. A. Zapffe and C. E. Sims. Dr. Weyl of Pennsylvania State College has been doing some work of this nature.

I. Discussion by W. A. Weyl and Samuel Zerfoss

Note on Evolution of Hydrogen from Iron as a Source of Chipping*

Since the experimental proof by Hoff and Klärding[1] and by DeBoer and Fast[2] that in certain cases hydrogen is released when chipping of enamels occurs, the H_2 content of the sheet iron must be considered to be a potential source of enamel defects. The following observations may supplement the work of Hoff and Klärding and may throw some light on the fundamental process of chipping due to hydrogen evolution.

(1) A container of ordinary sheet iron, enameled on the outside only, was filled with dilute acid (e.g., HCl 10%). Within a comparatively short time (from 30 minutes to several hours) at room temperature, chipping of enamel coat occurred. This indicated that some of the hydrogen, liberated through the action of the acid on the metal, is diffusing through the sheet iron and is released under considerable pressure.

FIG. 1.—Demonstration of hydrogen diffusion through enameling iron.

(2) A similar container, enameled only on the inside, was filled with pure water and the outside immersed in dilute acid. Under these conditions, not only chipping of the inside occurred but hydrogen bubbles evolved from inside the container and rose through the water, which confirms the observations of Hoff and Klärding.[1]

To study this phenomenon of hydrogen diffusion more thoroughly and to obtain quantitative data on the rate of diffusion, a simple apparatus was used (see Fig. 1). A sheet-iron cylinder, closed with rubber stoppers and tightly sealed, was connected with a water manometer. The cylinder was immersed in a bath of dilute HCl that was kept constant at 20°C. The stopcock was turned so as to establish connection with the manometer. Within a few hours, the pressure increased to 50 to 60 mm. of water, indicating that hydrogen was diffusing through the metal cylinder.

From studies of the diffusion of hydrogen through metals carried out by Ham,[3] we know that the diffusion speed depends on the temperature, pressure, and the reaction of the metal. Ham further established that hydrogen diffuses as hydrogen atoms and not as molecular hydrogen. From earlier work of Borelius and Lindblom,[4] we know that under conditions similar to those described herein, that is, when hydrogen is liberated electrolytically, considerable pressure may be obtained. The concentration of the hydrogen atoms due to the discharge of the ions corresponds to the effect of molecular hydrogen under pressure up to 1000 atm.

The observations of Hoff and Klärding[1] may be explained on a similar basis. In this case, however, the atomic hydrogen originates from the interaction of the iron surface with water liberated from the enamel melt while the ware is being fired. The hydrogen atoms readily diffuse into the lattice where they will form molecular H_2 when they collide, thus setting up a considerable pressure.

The real reason why enormous pressures develop between the iron and the enamel is that the rate of hydrogen diffusion through metal is much higher than that of hydrogen diffusion through a glassy phase. The order of magnitude of the two diffusion rates is known by the work of Taylor and Rast[5] and by that of Ham.[3] Similar phe-

*Received May 1, 1940.

[1] H. Hoff and J. Klärding, "Fishscaling Related to Gas Evolution in Enameling," *Stahl & Eisen*, 58, 914–16 (1938); *Ceram. Abs.*, 18 [5] 121 (1939).

[2] J. H. DeBoer and J. D. Fast, "Diffusion of Hydrogen Through Iron at Room Temperature," *Rev. Trav. Chim. Pays Bas*, 58, 984–93 (1939).

[3] W. R. Ham, "Diffusion of Hydrogen Through Nickel and Iron," *Trans. Amer. Soc. Metals*, 25, 536–64 (1937).

[4] G. Borelius and S. Lindblom, "Diffusion of Hydrogen Through Metals," *Ann. Physik*, 82, 201–26 (1927).

[5] N. W. Taylor and W. L. Rast, "Diffusion of Helium and Hydrogen Through Pyrex Chemically Resistant Glass," *Jour. Chem. Phys.*, 6 [10] 612–19 (1938).

nomena may be observed with two different metals, as in the case of the blistering of electroplated coatings, e.g., nickel-plated steel.

From a theoretical viewpoint, there are three ways to remedy this defect.

(1) The enamel may be changed to make it more permeable to hydrogen so that the diffusion coefficient in glass would approach the diffusion coefficient in metal.

(2) Hydrogen diffusion may be prevented by the use of an impermeable coating. This, for example, would mean the formation of a layer of gold or chromium oxide which are known to be impermeable to hydrogen. This procedure probably would interfere with adherence.

(3) Hydrogen diffusion into the iron lattice could be avoided by preventing the formation of free hydrogen atoms and by decreasing their stability or at least by reducing their concentration. This may be done by certain elements which are known to act as poisons in catalytic hydrogenation, such as phosphorous, sulfur, arsenic, and selenium.

II. Discussion by J. O. Lord

Recent developments in the knowledge of the behavior of hydrogen in steel have paved the way for the authors to study the effects of hydrogen on enamels on steel, which they have done in a masterly manner. It would be presumptous to make any offhand criticism of such a paper.

There has been a marked change in attitude of metallurgists toward the causes of defects in steel. Twenty-five years ago, oxygen was the root of all evil in steelmaking. When difficulties could be ascribed to no other cause, oxides were enlisted. This was a safe explanation because nobody knew much about analyzing for oxygen. Later, owing to improved analytical methods and new ingenious methods developed by Dr. Herty and others, we have learned more about the effects of oxygen, and in well-made steel the quantities we have to deal with are not impressive as causes of defects.

Nitrogen, likewise, did not last long as a refuse box for unexplained defects because it could be studied with comparative ease.

The expansion of the sheet industry has probably been responsible for the interest in the effects of hydrogen on steel because of the embrittlement of sheets during the pickling operation, but metallurgists in this case have approached the problem more cautiously and scientifically.

The agreement between the results of different investigators for hydrogen solubility in iron and the satisfactory correlation between the shapes of the curves and theoretical considerations leave no doubt as to the correctness of the assumptions of the authors. They have made it clear that hydrogen is capable of doing the things attributed to it.

This being admitted, I am impressed by the ease with which the problems of contradictory and anomalous enamel behavior seem to become unraveled. As pointed out in previous publications, what was sought was a chemical mechanism to account for the cyclic character of reboiling, the conditions necessary for adherence, and other characteristics of the enameling process. The authors have made a clear case for hydrogen in all of these.

Although they did not mention specifically the metallic dendrites found in the ground coats, their reasoning would apply perfectly inasmuch as they note the formation of Fe_3O_4 by a reaction between water vapor and the metal liberating nascent hydrogen. Certainly this is a reversible reaction by which metallic iron may be reprecipitated the next time the hydrogen is available.

The authors have cautiously refrained from placing hydrogen as the sole cause of defects, and I believe, with them, that it would not be right to make such an assumption. We should continue, unabated, the studies of the behavior of carbon gases and other chemical phenomena associated with enameling.

III. Discussion by J. J. Canfield

The authors are to be complimented on their excellent paper, their imaginativeness, which is stimulating, and particularly on the rather comprehensive bibliography that is attached. There are, however, a few points I would like to mention.

There is a question as to whether metallurgists, in general, accept the carbon-oxygen theory for the mechanism of reboiling. This may also be true for primary boiling.

There are some questions which naturally arise as to explanations of certain observations. The present suggestions are given to obtain some basis on which critical experiments might be made to determine the mechanism of such defects as reboiling or fishscaling.

The authors mentioned that rifts in the metal tend to increase the solubility of hydrogen. One question that arises then is the possibility for cold reduction of the metal to increase the rifts within the metal, which would increase the solubility of hydrogen and which, in turn, would make a sample more likely to show reboiling. The general observation has been that cold working decreases the tendency to reboil.

There has been an experiment performed several times in our laboratories in which metal samples were annealed at relatively high temperatures in a hydrogen atmosphere and cooled to room temperature in the hydrogen atmosphere. Our experience has been that these samples did not show reboiling, but we are unable to explain the reason for this.

Another question is that of primary boiling which, as we understand it, is a continuous evolution of bubbles during the firing of the ground coat, resulting in a roughened condition. If hydrogen is evolved to cause boiling, it is difficult to understand how it would continuously evolve at enameling temperatures where the solubility of hydrogen is considerably greater than at room temperature.

An observation on annealing of ground-coated samples has been that, if a ground-coated sample is cooled to room temperature after the first firing, it may reboil, whereas, if it is cooled only to 600°F. or annealed as glass is annealed at 800° to 900°F., it will not reboil on the first reheating. It is difficult to associate the effects of reboiling such as these with hydrogen as the only cause.

IV. Discussion by R. R. Danielson

A large amount of information and data on the properties and defects of enamels has been developed during the past twenty-five years, and certain valuable tools have been developed for correcting the defects. If we are to accept

the conclusions of the authors in their entirety, these tools must be discarded with little offered to take their place.

For example, Mr. Sweely did a fine piece of work at the Bureau of Standards some years ago on the correction of a chipping defect in the bottoms of enameled cookingware. This chipping occurs when certain enamelware containing water or other liquids is heated over a hot flame. Mr. Sweely showed that, regardless of the effect of hydrogen occluded in the metal, the chipping could be overcome by lowering the expansion of the cover enamels.

In enameling cast iron by the dry-process method, if the expansion is decreased, the enamel can be changed from one that crazes to an entirely satisfactory product. Further decrease in the coefficient of expansion may produce chipping. Similarly, in glazes on clay products, where there is no iron to consider and presumably no hydrogen, it is also possible to correct the defects of shivering and crazing when they are caused by differential expansion of the body and glaze.

The question arises as to the effects of hydrogen at temperatures where its pressure should be at a maximum. Twenty years ago, A. S. Cushman, a well-known metallurgical consultant, advanced the theory that gases in the metal would cause the defects of lifting or of fishscaling, and he pointed out that they had the typical bubble formation that would be expected if entrapped gas was pushing up the layer of enamel. It is difficult, however, to understand why this pressure exerts itself at room temperatures rather than at 400°C., where the volume of gas is much greater and the enamels are sufficiently viscous to show the effects of that pressure.

The authors have presented a fine exposition on the possible effects of hydrogen in steel. It clarifies many of the questions that have arisen as to the causes of the defects in enamels, such as blistering, reboiling, and, probably, certain isolated types of fishscaling brought about by poor enameling stock or abuse in pickling operations. If their conclusions are only partially correct, they have still made a valuable contribution to our literature on enamels.

V. Discussion by G. H. McIntyre

Various members of my staff have read this paper and they are enthusiastic about the findings.

The authors make the following statement:* "In seeking for a better understanding of the causes of enameling defects, one should list all possible causes instead of entirely omitting hydrogen from this list, as has so often been done, and one ought not only be careful to include it but to regard it as a most prominent suspect." The authors have thus indicated that they do not believe that all defects are entirely due to hydrogen but that we should look to hydrogen as a source of trouble. We are familiar with experiments on enameling sheets with ground coat on one side only, in which case the gas diffuses through the unenameled back and there are practically no defects on the surface.

Further experiments have shown that extremely large volumes of hydrogen are evolved from steel by heating the steel in vacuum at pressures of about 0.001 mm. of mercury. There is no doubt therefore of the possibility of hydrogen causing a great many defects.

In the matter of fishscaling, we are familiar with the effect of various types of ball clays in promoting this defect on ground coat. Chemically, however, we can determine no particular difference in the analysis of the clay to cause this phenomenon.

VI. Discussion by B. T. Sweely

This paper is a real contribution to the literature of the enameling industry. I agree with Mr. McIntyre that we should keep in mind the statement of the authors that hydrogen is one of the possible sources of the troubles that should not be overlooked. The effect of this paper on the enameling industry will be interesting to follow. There will be a decided tendency on the part of the investigators of enamel defects to take into account the work of these authors.

Hydrogen unquestionably is a factor in the development of enamel defects. As Mr. Danielson pointed out, however, it does not fit all of the conditions with which we must deal to overcome fishscaling or reboiling. There is the germ of a great deal of thought presented in this paper which I think will have a bearing on the future work of the investigators into the causes of the various defects encountered in enameling iron and steel.

VII. Discussion by Karl Kautz

(1) Fishscaling

The authors have taken up quite a large part of their paper attempting to relate hydrogen evolution from steel with fishscaling and blistering (reboiling is included in the latter classification). Hydrogen undoubtedly plays a part in some blistering, especially in cover-coat blistering. There are cases of fishscaling, however, in which hydrogen certainly does not contribute, and there are some facts about reboiling that cannot be explained by hydrogen evolution.

There are two (possibly three) distinct types of defects described as fishscales. (1) The first type spalls off in large semicircular areas, exposing a clean metal base, and it is almost always associated with poor adherence. This might be called the "true fishscale." (2) The second type (which may be a modification of the first) appears as tiny surface spalls or often as tiny surface fractures. They are quite irregular in shape and do not extend to the metal base but sometimes extend to the dissolved iron oxide layer of the ground-coat enamel. This type, which occurs on ground coats that adhere well to the metal base and often are regarded as being normally fired, is sometimes called "process fishscale." (3) The third type, called "shiner-scale" or "shiners," appears as tiny spalls or fractures of irregular area at the outer surface of the enamel, and they often have a sparkling appearance. They are generally associated with good adherence and an overfired condition.

Because enamels fired on iron are under great compression, the first type, or true fishscale, has often been thought to be caused by compressive stresses coupled with weak adherence. It is quite possible, however, that hydrogen, under certain conditions, may add its effect to those already acting and may tend to lift or separate the enamel from the metal.

The second type has also been explained as being caused

* *Jour. Amer. Ceram. Soc.*, 23 [7] 214 (1940).

by compressive stresses acting only in the outer layers of the enamel. The hydrogen would cause a rupture of the outer surface by hydrogen pressures which diffuse as far as the absorbed iron oxide layer but no farther.

The third type of fishscale, the shiner, has definitely been shown to be caused by overfiring or by saturation of the enamel layer with iron oxides and the formation of magnetite crystals (Fe_3O_4) in the enamel just below the outer surface. The shiner-scale does not lend itself to explanation by hydrogen pressure so easily as the first two. It can be eliminated in practice by applying heavier coats, by reducing the heat treatment, or by controlling the oxidation of the iron surface, for instance, with a thin film of metallic nickel.

Thus, of the three types of fishscaling, two might be influenced by hydrogen evolution from the steel, although compressive stresses undoubtedly still play a part. The third type (shiners) is caused by over-oxidation or saturation of the enamel with iron oxides.

(2) Reboiling

Blistering may have various origins, and hydrogen evolution undoubtedly causes it in some cases. Reboiling, however, should not be confused with blistering.

The research on vacuum annealing of sheet steel and the spectrographic analyses of the gases in steel mentioned by the authors was undertaken because it was believed that occluded gases were the cause of reboiling. This work proved that the gas evolution was caused, not by occluded gases, but by solid-phase reactions in the metal base.

Sheet steel with known reboiling tendencies was vacuum-annealed for days under a high vacuum at various temperatures, the highest just short of the melting point of steel. Some specimens were held under a high vacuum and heated to 2000°F. and then cooled to room temperature; this cycle was repeated many times.

Cobalt ground coats were applied without pickling the specimens. Reboiling was almost as severe on the variously treated specimens as on the original sheet steel. Certainly all hydrogen was driven out of these specimens under the severe vacuum treatments, and none could be occluded in pickling because they were not pickled. If hydrogen is occluded from the 1% of H_2O remaining in the dried slip, there can be no hope of overcoming reboiling, yet now there are several ways to prevent it.

The gases, furthermore, evolved under a high vacuum when the sheet-steel specimens were heated, were constantly observed with a visual spectroscope. Hydrogen lines were observed only on the first heating of the specimens and these lines disappeared at about 1200°F.; thereafter only carbon monoxide lines were observed. When these specimens were cooled to room temperature, always under vacuum, and then reheated, no hydrogen lines were observed—only CO lines, which proved that occluded hydrogen had been eliminated from the specimens.

Another experiment is enlightening. When reboiling sheet steel is severely scaled, or oxidized, in steam at 1500°F. until a deep scale is produced and this scale is then reduced in hydrogen at the same temperature, reboiling does not take place. According to Zapffe and Sims, the steel should take up a large amount of atomic hydrogen during the steam scaling from the reaction,

$$Fe + H_2O \longrightarrow FeO + H_2.$$

(Note: FeO scale formed first at this temperature altering slowly to Fe_3O_4 scale at the outer surface.) To make matters worse, the scale was then reduced in hydrogen (molecular) from which some additional hydrogen was probably occluded.

These specimens were not pickled because a carbon-free coat of iron was desired. They did not reboil. One half of one specimen was immersed in concentrated HNO_3 until the carbon-free skin of iron was removed; that half showed reboiling. The carbon-free skin of iron was removed with coarse emery paper from one half of another specimen; that half also showed reboiling. How can this be explained? Certainly not by hydrogen evolution. Here was sheet steel saturated with hydrogen, but it did not reboil. This oxidation in steam and reduction in hydrogen (in addition to saturating the steel with hydrogen) produced a skin of carbon-free iron at the surface which did not cause reboiling because there was no carbon present to form carbon oxide gases.

The hydrogen evolution theory of reboiling is refuted in another experiment wherein reboiling sheet steel is plated galvanically with nickel and it does not reboil. It is not necessary to use nickel in this case. Pure iron, electroplated on reboiling sheet steel from a solution of ferrous ammonium sulfate, will stop reboiling. If oxidation of carbides produces the gases which cause reboiling, then plating pure iron on the surface should, and does, stop reboiling. If hydrogen evolved from the iron base causes reboiling, then plating the surface with pure iron, or nickel, should make no difference in its reboiling characteristics.

Despite the fact that hydrogen becomes more soluble in iron with increase of temperature, Zapffe and Sims believe that sufficient quantities of hydrogen escape during heating to cause reboiling. If this is true, then the reverse, the slow cooling of an enameled specimen from 1600°F. through the viscous range at 1100°F., should cause violent reboiling, because with a decrease in temperature, hydrogen becomes more insoluble in iron and even larger amounts should escape than upon heating. Repeated attempts to produce reboiling by cooling enameled specimens through the highly viscous range around 1100°F. have never been successful.

Another point in this theory is that hydrogen, collecting in blisters between the iron base and the enamel layer, is supposed to be reabsorbed by the metal base as the temperature of the specimen increases and the viscosity of the enamel decreases. When atomic hydrogen leaves the steel to form these blisters, it should combine to form molecular hydrogen. The authors tell us that steel is very impervious to molecular hydrogen, which does not begin to dissociate until a temperature of 1472°F. is reached. How then could the gases in a reboil blister be reabsorbed at 1100°F. or at 1200°F.?

Not forgetting that the gas in the reboil blister may be CO instead of hydrogen, another mechanism for the apparent collapse of the blister (without bursting) must be found.

It must be remembered that the viscosity of the enamel changes rapidly from its softening point up to about 1200°F., and the top of the blister becomes thinner and thinner as the viscosity decreases. A thickness and fluidity of enamel is eventually reached wherein diffusion of any

gas, whether it is CO, H_2, N_2, or CH_4, is very rapid and the blister collapses without bursting. An explanation of this nature may fit the facts better than one of reabsorption of the gas into the steel, especially if molecular hydrogen is concerned.

One conception of reboiling must be clarified. Generation of gases at the surface of the iron takes place at all temperatures (not specifically at 1100°F.) during heating because diffusion of iron oxides and iron carbides in iron is greatest during the heating cycle. This diffusion is arrested on chilling or cooling, but it begins on heating. Reboiling, therefore, is but a continuation of primary boiling and manifests itself only when the temperature of the enamel is between 1000° and 1200°F. Most enamels in this temperature range are extremely viscous and accumulated CO gas pressures generated by heating up to this point are relieved by blistering the softened coat of enamel. These blisters are large enough to be seen by the unaided eye. The gas-generating reactions do not cease at 1200°F. but continue as the metal-enamel system increases in temperature. Above 1200°F., the fluidity of the enamel is so greatly increased that the gases escape continuously as very minute bubbles, invisible to the unaided eye, but visible easily at 25 or 50 diameters magnification.

I am not trying to belittle the excellent work of Zapffe and Sims, but I am citing a few instances wherein defects result from causes other than by hydrogen evolution. I believe hydrogen evolution might explain many cases of cover-coat blistering, such as the "cluster type" and "isolated type" and even "scratch blisters." I believe it also plays a role in some cases of blackspecking and copperheading. The first two types of fishscaling possibly could be explained by hydrogen evolution in conjunction with compressive stresses.

The two defects, however, that cannot be explained by hydrogen evolution are shiners and reboiling. These are both primarily the result of oxidation.

VIII. Discussion by A. I. Andrews and B. W. King, Jr.

A. I. Andrews

We are very much interested in this paper, and several men in our laboratory have studied it quite thoroughly. Most of the remarks were, "I think they have something there," and we still feel that way about it.

With any new idea like this, there is always a tendency, however, to carry it a little bit too far. We must be careful not to try to explain everything on the basis of a new idea, which often becomes a pet, and to the exclusion of older theories.

We checked some of the experiments, and B. W. King in our department ran a few experiments which he will present.

B. W. King, Jr.

A check was first made on the test whereby a pan from which the enamel had been scraped on the inside was filled with dilute sulfuric acid. In a short time, the enamel chipped from the outside. It was thought that the scaling noted might possibly have been the result of the way in which the enamel had been removed. Two identical pans were then de-enameled on the outside with molten sodium hydroxide; one pan was placed in hot acid and the other in a hot alkaline solution. In a short time, the pan in the acid solution began to fishscale on the inside, but no change was noted in the pan placed in the alkaline solution. These results agree with those of Zapffe and Sims. We did not determine whether or not a gas actually penetrated the metal, or assuming that it did, the identity of the gas. The explanation of Zapffe and Sims, however, seems to be reasonable.

The second experiment was run on the action of hydrogen in high-carbon steels. Some time ago, Badger and King[1] found that if a piece of 1/4-inch drill rod containing about 0.70% carbon was heated in hydrogen, it could be enameled without blistering. The explanation appeared to be that the treatment had decarbonized a layer from 0.001 to 0.002 inch thick on the surface of the rod. According to Zapffe and Sims, "hydrogen is retained by carbon in steels, probably in the form of a quasi-methane structure." According to their experimental work, furthermore, so thin a decarbonized layer should have practically no effect on the rate of hydrogen diffusion, as hydrogen was found to diffuse quite readily through much thicker sections. It was therefore hard to see why our experiment stopped blistering, unless hydrogen had been removed from the rod in addition to what little might have been released by the removal of the carbon at the surface.

Our next experiment was to try to remove hydrogen from the steel and to avoid the introduction of more hydrogen during the enameling process. A piece of drill rod was first heated in vacuum for about one hour and forty minutes at 950°C. so that all hydrogen not actually dissolved in the metal would be driven off. The sample was allowed to cool slowly, still under vacuum, so that as the solubility of the hydrogen decreased, more of the gas would be removed. The drill rod was next sandblasted, dipped in enamel slip, and placed at once in a drier. It was dried first for one-half hour in vacuum at 150°C., then for another half hour at about 220°C., and was fired in air for five minutes at 820°C. The rod was found to blister badly; the precautions taken to remove hydrogen apparently had no beneficial results. The results thus appear to contradict the theory that the blistering of high-carbon steels is due solely to the presence of hydrogen because, when the specimen was first heated in hydrogen, blistering was eliminated; and when hydrogen concentration was eliminated, or at least decreased, blistering was encountered.

IX. Discussion by J. E. Rosenberg

This paper is well worth studying, although I cannot believe that any important part of enameling defects is due to hydrogen in steel. It is unfortunate that it is difficult, in fact, impossible to determine hydrogen in steel without the use of special and expensive equipment. Even under the best conditions, small amounts, such as would be found in enameling stock, would not be determined. Under these circumstances, the deductions are based on assumptions which can neither be proved nor disproved. Although the experiments cited by the authors demonstrate well-known

[1] A. E. Badger and B. W. King, Jr., "Remove Carbon from Iron and Steel by Heat Treatment," *Ceram. Ind.*, 29 [1] 41 (1937).

facts concerning the properties of the hydrogen–iron system and the mechanical effects which may result therefrom, they do not prove that hydrogen is present in iron during normal enamel practice.

I have not read much of the literature on the subject of hydrogen in steel, but I have examined some of the papers cited and have found no data to indicate that American enameling stock contains hydrogen.

Enameling iron, melted in the open-hearth furnace, is covered by a slag which prevents the action of the furnace atmosphere on it. The steel bath must also be kept oxidizing to bring the carbon down to the low point necessary in this grade of steel. I am not sure about the possibility of hydrogen remaining in an iron in which any quantity of oxygen, probably in the form of iron oxide, has dissolved in it.

In casting the ingot, the steels are rimmed, that is, the steel cools slowly from the outside so that the gases escape from the center of the ingot as cooling takes place. During the rolling of the ingot to sheet and the normalizing of the sheets, the steel is in an atmosphere which has little or no hydrogen, and it has every opportunity to come to equilibrium with this atmosphere.

Hydrogen is absorbed by steel during pickling, but it is as easily eliminated by immersing the pickled sheet in hot water for a few minutes.

Inhomogeneities in steel during pickling may possibly cause the capture of hydrogen which may give rise to difficulties. I have noted blisters raised in certain steels when pickling acid is used that contains hydrogen sulfide. The blisters undoubtedly are caused by the pressure of hydrogen gas, but I am not clear as to the role played by hydrogen sulfide. In one case, the blisters appear only on one face of the steel sheet, which might indicate that the defect is in the structure of the sheet. From time to time we have sought to overcome enamel difficulties which seemed to be due to the evolution of gas during the firing process, and the possibility of hydrogen was considered. To eliminate this possibility, the steel was pickled in acid containing an inhibitor, which prevents the formation of hydrogen during pickling. This method, however, did not reduce the difficulty, indicating that hydrogen was not at fault.

The enameling industry, generally, does not use inhibitors in the pickle acids although they have been tried from time to time. If the evolution or atmosphere of hydrogen was the cause of the difficulty, inhibitors would have found their place in this industry.

The third possibility of getting hydrogen in the steel is during the firing of the ground coat in the enameling furnace. In normal and even in fairly extreme conditions, the water vapor in the furnace atmosphere hardly exceeds 3%. Water vapor, reacting with the iron, might give rise to hydrogen, but the maximum pressure of the hydrogen would be that of the water vapor, that is, about 0.03 atmosphere. The solubility of hydrogen, however, depends on the pressure, so that the absorption of hydrogen from this source is not very great.

X. Discussion by F. R. Porter

Assuming that the steel companies *can* make steel free from holes and inclusions (if hydrogen is at fault and might be trapped) and that the steel companies can furnish a satisfactory product, steel probably must be pickled twice in the processing.

I hope that Dr. Zapffe will give us his ideas as to how the enamel shop might change its pickling procedure to alleviate or cut down the amount of hydrogen that might be absorbed. His reference to this in his paper is not very clear as to the time, temperature, or the changes he made when he referred to the pickling procedures on the $^1/_8$-inch rod.

XI. Discussion by G. H. Spencer-Strong

I am particularly interested with the references to cast-iron difficulties as possibly attributed to hydrogen. The manufacture of cast iron in itself should give rise to the solution of considerable quantities of hydrogen in the cupola. Pouring cast iron into green molds, not properly vented, might also increase the amount of hydrogen. The use of the bull ladle and double pouring the iron from the cupola may help to eliminate some of these trapped gases.

We shall probably have several papers bearing on this subject because some nice fields are opened up and there are anomalies between past work which has been reported and the present paper.

I wish to congratulate the authors on this work.

XII. Discussion by Louis Navias

The authors have made a special point of showing that the hydrogen dissolved in steel occurs in the atomic, not in the molecular state. In Figs. 1, 2, and 3, however, they definitely give the molecular formula of hydrogen. This matter should be clarified. Some of the later figures merely state hydrogen to be a diffused gas without indicating whether it is in the atomic state or in the molecular state.

REPLIES BY C. A. ZAPFFE AND C. E. SIMS TO DISCUSSIONS

I. Reply to W. A. Weyl and Samuel Zerfoss

Weyl and Zerfoss have developed some interesting proof of the hydrogen theory described in the present paper. Clarification of a few points seems advisable in view of the broad study of hydrogen in steel now being conducted at Battelle Memorial Institute.

(1) It is better not to stipulate a limit of 1000 atmospheres as the equilibrium pressure of molecular hydrogen during electrolysis. Much greater pressures are obtained every time that steel is embrittled or fissured by hydrogen absorbed electrolytically. The theoretical equilibrium pressure of molecular hydrogen calculated from the Nernst formula for ion deposition is of the order of 10^{20} atmospheres.

(2) The picture of atoms colliding within the lattice should not be made confusing. The enameling defects in question are caused when the hydrogen effuses from the steel, and its previous condition within the steel is irrelevant except for aspects discussed in the paper.

(3) The comparison of diffusion rates through metal

and through enamel should be made only with recognition of the fact that the two mechanisms of diffusion are entirely different; the one necessitates dissociation and diffusion as atoms through the metal lattice, whereas the other is simply molecular diffusion. It may be better to say that defects develop when the hydrogen cannot be removed through the enamel as rapidly as it effuses from the steel. In the case of electroplate, Weyl's statement is entirely correct.

This differential in diffusion has underlain, perhaps inadvertently, many historical changes in enamel composition and firing procedure. The problem has an obvious solution, pointed out by Weyl in his first proposed remedy. The second remedy, however, would be inadvisable for other reasons than those mentioned, for such a coating would aggravate defects caused by hydrogen already present in the steel when the coating was applied. The third remedy must be cautioned against, for those elements that poison catalytic hydrogenation also act to increase hydrogen absorption by steel as much as one hundred times in some cases[5,4].*

II. Reply to J. O. Lord

Lord aptly pictures the indecisions of metallurgists regarding gases in steel. Hydrogen has been the most elusive of the gases, and, in truth, it appears to be the only common element that behaves as a gas in steel, at least at ordinary temperatures. As for the metal dendrites sometimes found in ground coats, the authors agree that these dendrites represent a precipitation and that a likely reaction is reduction of iron oxide by hydrogen.

III. Reply to J. J. Canfield

Canfield has raised an important question as to the effect of cold working. Deformation actually aids the escape of hydrogen already present in steel principally because rifts are opened that permit atomically dissolved hydrogen first to precipitate internally as molecules; when the molecular pressure in these rifts is sufficient, the molecules may escape through adjoining rifts until a significant portion ultimately leaves the specimen. Subsequent pickling must supply hydrogen to these rifts as well as to the iron lattice so that the absorptive capacity of the steel has been significantly increased by the deformation. If care is taken, however, to avoid subsequent absorption or to remove hydrogen preliminary to firing, cold-worked material may be expected to show less tendency to develop hydrogen-caused enamel defects. Deformation opens the structure so that hydrogen diffusion both in and out is facilitated. The early part of the heating period, of course, removes the effect of the cold working.

Canfield's second question refers to annealing and cooling in a hydrogen atmosphere. It is commendable that he says that he "is not able to explain it," for this is the type of evidence that has so often been erroneously advanced as a contradiction of the hydrogen hypotheses. If a piece of steel is annealed in hydrogen at some high temperature and quenched or rapidly cooled in or out of hydrogen, enamel cannot be applied without almost complete destruction of the coating. If, however, the piece is slow-cooled, the hydrogen atoms will diffuse out of the steel regardless of the molecular hydrogen in the atmosphere, because a pressure of only one atmosphere of molecular hydrogen is so ineffective in supplying atomic hydrogen to steel below about 400°C. (752°F.) that in the best vacuum there would be no important difference.

Canfield's third question concerns an apparent contradiction between primary boiling and known hydrogen solubility. In the present paper, the authors have stated that occluded hydrogen "may cause or contribute to" primary boiling. Numerous other gases may also be evolved during this initial firing, most of them depending on the composition of the enamel. Hydrogen will only effuse from the steel at enamel firing temperatures if the gas is occluded in the steel under greater pressure than it exists in the adjacent atmosphere. Extension of the present work[9] has led the authors to believe that one of the most important sources of hydrogen that may outweigh all other sources is the water that is chemically combined in the slip. Only part of this water may be available for reaction with the steel, and part, probably most, of the resulting hydrogen will be absorbed by the steel. Gases liberated during the primary boiling would then conceivably consist of water vapor, some hydrogen, methane and carbon oxides, if carbon is present, plus decomposition gases from some of the unstable chemicals in the slip.

Regarding the effect of cooling on reboiling, Canfield points out that the specimen generally must cool to room temperature to show reboiling on subsequent heating. This phenomenon is explained in the present paper for the case of isolated reboiling over heterogeneous sections of the steel. Reboiling in general can be explained similarly, that is, slow cooling to room temperature may eliminate reboiling because critical quantities of hydrogen may be eliminated. Normal cooling is more rapid and favors retention of hydrogen and therefore reboiling. Annealing at glass-annealing temperatures may eliminate hydrogen if the gas can pass through the enamel. Lastly, on cooling only to 600°F. before reheating, supersaturation may not yet have developed, and heating would have no tendency to drive the hydrogen out of the steel (see reply to Kautz). The subject of reboiling will be more carefully considered in a later publication,[9] for it is not fair to judge situations on the basis of the incomplete evidence at hand. In the meantime, care should be taken not to dismiss consideration of hydrogen because relations are not immediately obvious.

IV. Reply to R. R. Danielson

Danielson mentions Sweely's work in which chipping was corrected by adjusting the enamel composition. Perhaps there was a simultaneous increase in adherence or in permeability of the enamel for hydrogen. Figures 6 and 38 in the present paper show experiments that demonstrate how slight heating greatly accelerates hydrogen effusion and thereby simultaneously aggravates chipping or fishscaling. The role of mechanical stress in causing fishscale-type defects is questionable in the minds of the authors. Cracking in the enamel on the graphite specimen in Fig. 29 is plainly due to thermal or mechanical stress. Crazing and hairlines are also defects that one should expect from differential contraction on cooling; but a fishscale or a small chip, explained as being due to mechanical stress, would seem to necessitate localized heterogeneities in the enamel or on the steel surface that do not exist. Expansion stresses may weaken adherence

* See references, p. 300.

of course, and thereby aggravate the tendency to fishscale, but localized aerostatic stress from hydrogen effusion appears to be the most probable direct cause of many of these defects.

The question on temperature is not quite clear. The aerostatic stress from temperature-expanded hydrogen should not be compared with the stresses under consideration for equilibrium pressures of molecular hydrogen, for the latter are much greater and are assumed to be responsible for the defects in question. At 400°C. (752°F.), the nature of enamel is not so well fitted either for scaling or blistering. Figures 1, 2, and 3 show that at this temperature hydrogen dissolves reversibly in steel and that equilibrium is rapidly attained. Enameling stock need not contain more than a small amount of hydrogen to cause enameling defects, and this amount may likely stay in solution at 400°C., especially because the enamel forms a protective coating that will tend to surround the steel with pure hydrogen under pressures that could considerably exceed one atmosphere, which, in turn, would increase the solubility. At temperatures below 400°C., however, supersaturation quickly sets in even for most dilute solutions, and the equilibrium pressure of molecular hydrogen underneath the enamel may become too great for the strength of the coating. Movement of hydrogen in and out of cavities in steel or in and out of the steel itself is only a matter of shifting equilibrium based on concentration changes of atomic hydrogen and can be explained on the basis of the information contained in Figs. 1, 2, and 3.

V. Reply to G. H. McIntyre

McIntyre mentions the relation between fishscaling and various types of ball clays. The only statement that can be safely made is that different clays may contain different water contents, which should have an effect on the charging of the steel with hydrogen during firing and in the development of the oxide layer. Differences in adherence and permeability to hydrogen of the resulting enamels also should lead to differences in the tendency to fishscale.

VI. Reply to Karl Kautz

Kautz identifies three types of fishscales, but he grants that hydrogen may be a cause only of the first two. Such a distinction seems unnecessary for reasons already advanced in replying to Danielson. The authors have assumed that the mass of tiny hydrogen-caused fishscales on the plate in Fig. 38 are "shiners," and Kerstan (reference 199) has demonstrated that "shiners" are merely small fishscales and hence are caused by hydrogen. Kautz has granted that the distinction between "true fishscales" and "process fishscales" is that hydrogen in the latter defect probably has diffused as far as the iron oxide layer before rupturing stresses developed and that the three types represent, in order, an increasing degree of firing. Why, then, make an orphan of "shiners"? The presence of undue amounts of iron oxide in enamel showing this defect attests to hydrogen absorption from moisture reactions; the relation to overfiring may be that a glazed layer has formed on the surface that is particularly impermeable to hydrogen so that the gas would cause rupture only at the very surface. Figures 39 and 40 show on one specimen the progression of all the defects outlined by Kautz. Hydrogen is the sole cause of the defects in these figures, and the variations in effusion of the gas and nature of the enamel have provided the characteristic distinctions.

The authors are not yet prepared to discuss all the ramifications of the phenomenon of reboiling. From information in the present work, however, the following facts are important to face.

(1) The authors do not believe that the spectrographic studies to which Kautz refers prove that gas occluded in the steel is not responsible for reboiling. The studies only prove that occluded hydrogen could not cause *primary* boiling in those particular specimens, but primary boiling is not mentioned. Primary boiling, however, could also have occurred in these specimens, as described in the reply to Danielson. The fraction of hydrogen that is absorbed during firing from the seemingly innocuous 1% of H_2O in the slip is surprisingly efficacious in causing subsequent defects of reboiling and fishscaling types. There are several ways to avoid reboiling, as Kautz points out. The most certain methods, however, eliminate absorbed hydrogen and prevent subsequent absorption. The effects of annealing and slow cooling are well known, and their application will be discussed later.[g] Some ware does not require precautionary measures because conditions of the enamel, of the steel, or of both are not conducive to developing sensitivity to reboiling. Results of such tests should not be used indiscriminately to contradict the results of other tests. Although carbon oxide gases are likely to be present in reboiling gases when carbon is present on the surface of iron, it is impossible to explain reboiling as a function of carbon oxidation. Reasons have been given on pages 18 to 22 of the present paper. If carbon-oxygen reactions play a significant part in causing enameling defects on sheet steel, then it should be virtually impossible to enamel cast iron. Yet cast iron is successfully enameled, and a publication appearing shortly[d] shows that the appearance of boiling or pinholing phenomena in cast-iron enameling is a function of the amount of hydrogen in the casting and that when hydrogen is absent no boiling whatsoever occurs. The presence of other gases in the boiling effusion must be expected, for numerous minor gas reactions may accompany the fusion of enamel. To reappear, however, during subsequent firings, these gases must settle some place, and the only reasonable collecting place, fitting known facts, is in the steel itself. Hydrogen is the only gas that behaves as a gas in steel at ordinary temperatures, and its known functions fit admirably into the picture of reboiling.

(2) The scaling and de-scaling experiment appears contradictory to the hydrogen theory, but it may be answered according to the reply given Danielson on annealing in hydrogen. The fact that Kautz does not report complete destruction of the enamel coating from hydrogen effusion during firing indicates that hydrogen was not retained in the steel by the treatment. Perhaps the piece was slowly cooled or subsequently baked or was so thin that the hydrogen dissipated at ordinary temperatures before firing. The insufficient data prevent drawing further conclusions. That removing the carbon-free skin caused reboiling may be clarified by referring to the specimen in Fig. 30, wherein hydrogen held by the carbon caused boiling when the carbon was exposed or close to the surface; the specimen in Fig. 37, however, under similar conditions, showed no boiling

on the front side of the plate, although hydrogen was liberated during firing from the carbon that lay underneath along the diagonal on the back face. That the hydrogen finally did reach the surface was attested by the appearance of fishscales some days later. Another aspect of this problem is presented in discussing King's experiment.

Kautz's experiment with galvanized and electroplated coatings is puzzling to the authors, for electroplate often contains a great deal of hydrogen. In fact, the reboiling phenomenon known as "scratch blisters" seems to be due to such hydrogen,[f] as Kautz suggests. Scott (reference 73) found that enamel boiled badly on copper-coated iron, whereas copper itself gave no trouble. Such contradictory evidence should be carefully studied before a conclusion can be drawn.

The reboiling that Kautz expects at 1100°F. during cooling does not follow from the hydrogen theory, as partly explained in replying to Canfield and Danielson. It must be remembered that the solubility curve in Fig. 1 is only for external molecular hydrogen under one atmosphere of pressure and that as the hydrogen concentration under the enamel layer changes the solubility changes. Reboiling could occur on cooling only if the steel becomes supersaturated with hydrogen during cooling; and even if the enamel were fired in pure hydrogen it could not be definitely stated that the steel was saturated, for there are two important factors in establishing the effective equilibrium pressure, (*a*) the water reaction at the steel surface and (*b*) the protective nature of the enamel coating. Because interface concentrations are not known, the conditions for supersaturation can only be surmised. Thus, even if a specimen were fired in pure hydrogen, the protective nature of the enamel coating might allow the hydrogen pressure under the coating to increase as the enamel cools, which would countereffect the tendency to supersaturate. It is the supersaturation occurring at lower temperatures (below about 400°C.) that is apparently most effective, an assumption corroborated by fishscaling. The solubility decrease from enamel firing temperatures to 400°C. is only severalfold, but from there down to room temperature the decrease is some unknown value that is many times greater. Diffusion, however, is too slow to relieve the supersaturation that develops at these lower temperatures, and the enamel is sufficiently impermeable so that hydrogen gathers at the interface under pressure which may or may not be sufficient to cause scaling. On reheating, the tendency to fishscale is aggravated from sudden increased effusion and expansion of this gas, and this blends into reboiling when the enamel melts before the steel can come to temperature and equilibrium can adjust itself. Areas showing fishscaling develop reboiling.[g]

According to the hydrogen theory, then, reboiling during cooling need not be expected. How can the carbon-oxide theory account for a reaction during successive heatings without postulating a similar reaction on cooling?

Regarding re-solution of hydrogen at 1100° to 1200°F., discussed by Kautz, the authors have stated that hydrogen re-solution "first becomes fairly rapid" at 800°C. (1472°F.). This fact can be ascertained from the sudden increase in solubility shown in Fig. 1, beginning at 800°C. Depending on surface concentrations, however, some re-solution may begin at temperatures as low as 400°C., where absorption first becomes reversible. Re-solution at 700°C. (1292°F.), for example, is so important that this temperature is unfitted for relieving "flakes" in steel and embrittlement in weld metal.[e]

Kautz explains reboiling as a phenomenon depending on diffusion of iron oxides and carbides in the steel, and he states that the arrest of the chemical reaction on cooling is the only division between primary boiling and reboiling. The mobility of carbon in alpha iron, however, is exceedingly low, and enameling stock contains such a minimum of carbon that the highest firing temperature scarcely attains the transformation temperature. Many hours are required to decarburize ordinary steel even at a temperature as high as 900°C. (1652°F.). The few minutes that enameling steel is at firing temperatures considerably below this could not possibly be sufficient for significant diffusion of carbon. In any event, the reaction would be most pronounced at the maximum temperature and not at 1100° to 1200°F. Diffusion, furthermore, is a temperature function and should not occur preferentially on heating. Finally, tests with cast iron, where there is every chance for carbon-oxygen reactions, showed no reaction up to 1350°F. when hydrogen was absent.[d,e]

VII. Reply to A. I. Andrews and B. W. King, Jr.

Andrews' caution regarding carrying a new idea too far is well placed, and the authors wish to emphasize again that the present refutation is not designed to discourage thinking along other lines but to bring the most careful attention to bear on a subject whose elements have wide importance and are extremely elusive.

King's experiments with high-carbon steel are interesting. An opinion now would be premature, but some pertinent remarks may be made. First, the authors grant that carbon-oxygen reactions may be significantly effective at temperatures not below 1350°F. and that higher temperatures will favor the reaction. There was a great deal of carbon present in King's specimens and the firing temperature was probably high. No information is given as to whether the specimens reboiled or at what temperature blistering began. The two specimens in Fig. 30 each blistered over the high-carbon areas, but even then it was concluded that hydrogen was largely to blame for reasons to be given soon. Granted that carbon oxides may have caused some of the reaction in King's experiments, another reaction that has been largely overlooked is the decarburization of steel by hydrogen. The hydrogen liberated by the water reaction is twice as abundant as the oxygen, it is in an extremely active form, and it is a known decarburizer that is more effective than pure oxygen, which largely depletes itself forming a compound with iron. Thus, the carbon-free case may have permitted the hydrogen liberated by the water to dissolve in the iron, whereas the presence of carbon in the other experiments caused immediate formation of methane which is insoluble and leaves the steel, evidenced as decarburization. In discussing Fig. 30, it was pointed out that tiny brilliant sparks attended each bursting blister, from which it was assumed that the gas in the blister contained methane.

The relation of hydrogen to carbon in steel is speculative, but one point is rather clear. The "quasi-hydrocarbon" that has been suggested is a result of hydrogen *already in the steel* from saturation at some high temperature being

restrained from effusing at lower temperatures by carbon, which is likewise in supersaturated solution but much less free to move. Although steels may show supernormal hydrogen retention when carbon is present, less hydrogen is actually able to dissolve into steel when carbon is present. Hydrogen and carbon are so reactive that when they contact one another in steel methane is formed as postulated, and at high temperatures the methane escapes to cause decarburization, whereas at lower temperatures it cannot escape and fissuring may result.[a] If a carbon-free case surrounds the cementite during enamel firing, the hydrogen from the water reaction may diffuse into the steel, but it cannot effuse as methane in the limited firing time. An extended firing time would certainly cause blistering on that steel if the piece were fired in hydrogen, for decarburizing involves formation of a gas and the gas would have to escape through the enamel. Whether sufficient hydrogen is absorbed from the water reaction to act noticeably in that manner would have to be determined by experiment.

VIII. Reply to J. E. Rosenberg

Rosenberg interprets the present work in a manner that is somewhat surprising to the authors. The fact that hydrogen analyses to date have been so inconclusive is responsible for the great oversight in identifying the activities of this gas. Expensive equipment is not as necessary as a knowledge of how to use the equipment and how to interpret the results; and it has been shown in the present work that analyses actually prove that hydrogen is not only the generally predominating gas in steel but that it is also probably the only element that is a gas in steel. No analyses were attempted in the present work because the experiments shown in Figs. 16 to 40, inclusive, demonstrate without much question that the defects under consideration have been caused only by hydrogen.

Regarding absorption of hydrogen in the open-hearth furnace, a great deal has been written,[a] and it has been proved that the hydrogen content of open-hearth steel is often sufficient to develop steel-rupturing pressures, which are considerably greater than the pressures necessary to chip or blister enamel. The many other sources of hydrogen, however, which have been discussed both in the present paper and elsewhere,[a,f] may completely mask the effect of inherent hydrogen so that absorption in the open hearth is inconsequential. The firing operation itself is last and is the most important. The fallacy of ridding hydrogen by heating in boiling water formed the basis of the present paper. The action of hydrogen sulfide in the pickling liquor, mentioned by Rosenberg, forms the basis of other work by the author.[h] Briefly, hydrogen sulfide can increase hydrogen absorption by steel fifteenfold. Inhibitors reduce visible hydrogen evolution but have unexpected effects on hydrogen absorption,[g,h] so the test made by Rosenberg does not prove that hydrogen was not to blame. Inhibitors in enameling practice would introduce other complications which make them inadvisable. Lastly, the partial pressure of hydrogen in the furnace atmosphere during enamel firing has but little to do with hydrogen absorption from reactions at the steel surface.

IX. Replies to F. R. Porter, G. H. Spencer-Strong, and Louis Navias

Porter's question on hydrogen absorption from pickling will be covered in a subsequent publication.[h]

Spencer-Strong rightly suspects hydrogen troubles in cast iron, and his work over the past several years carried implications that had much to do with developing proof of the hydrogen theory in the Battelle laboratories. This work will be published shortly.[d,l]

In regard to Navias' suggestion for standardizing the designation of hydrogen in steel, it certainly would be preferable from a chemist's viewpoint to express hydrogen absorption in atomic percentage, for the system is an alloy of hydrogen atoms and iron atoms. Analyses, however, are commonly expressed in terms of molecular hydrogen, and the authors have felt that they have made a long first step already by criticizing the use of weight percentage.

The authors, in conclusion, wish to acknowledge the kindly comments and the many interesting viewpoints that have appeared in the foregoing discussions. Whether or not the present work is of direct use to enamelers, it is hoped that future investigators will consider carefully the elusive functions of this gas as an important feature in every industry where steel or iron is used.

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(*d*) With C. E. Sims, "Cause of Pinholes and Some Related Defects in Enamel Coatings on Cast Iron" (to be published in *Jour. Amer. Ceram. Soc.*).

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(*h*) With J. L. Yarne, "Hydrogen Absorption by Steel During Acid Pickling and Cathodic Electrolysis" (to be published).

(*i*) "Cause of Some Defects in Sheet Steel" (to be published).

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BATTELLE MEMORIAL INSTITUTE
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ATOMIC CONSIDERATION OF IMMISCIBILITY IN GLASS SYSTEMS*

By B. E. Warren and A. G. Pincus†

Abstract

An attempt is made to apply the ideas of crystal chemistry to the problem of immiscibility in glass systems. Miscibility is favored by the tendency of the network-forming cations, Si, B, and P, to bond with all available oxygens in the melt. Immiscibility is favored in compositions which do not allow the other cations, such as Na^+ and Ca^{++}, to be properly surrounded by unsaturated oxygens. The importance of this effect may be related to the valence and size of the cation. A qualitative discussion is given for a number of binary and ternary systems.

I. Introduction

The following discussion is an attempt to correlate some of the well-known facts of miscibility and immiscibility in glass systems with the present-day concepts of structural silicate chemistry. It is assumed that the atomic arrangement in the glass melt is roughly the same as in the glass, except for the obvious difference that in the melt bonds are continually breaking and reforming. The tendency of a glass melt to remain as a single phase or to segregate into two phases may then be discussed qualitatively in terms of the factors which stabilize the various possible structures. At the present stage, the theory is not able to predict with certainty what will happen for a given composition, but it is possible to correlate many of the observed facts.

The atomic bonding in the glass is pictured as largely ionic. The electrostatic bonding energy then is given by the equation,

$$E = \frac{-z_1 z_2 e^2}{R_{12}}.$$

Wherein z_1 and z_2 = valences.
R_{12} = atomic separation.

The magnitude of the bonding energy increases with the valences and decreases with the sizes of the atoms. The Si-O bond is extremely stable because the valences are 4 and 2 and the silicon-oxygen distance, 1.62 A, is very small. At the other extreme, the Na-O bond is relatively weak, as the valences are only 1 and 2 and the sodium-oxygen distance, 2.35 A, is rather large.

In glass-forming systems, the oxides may be divided into two classes, namely, network formers and modifiers. The network formers, SiO_2, B_2O_3, and P_2O_5, are those for which the magnitude of the cation-oxygen bond energy is large. The glass builds up a structure which will satisfy as well as possible the requirements for the network-forming cations. The other class of oxides, such as Na_2O and CaO, has considerably smaller cation-oxygen bond energies. In a glass structure, these cations get only a second choice in satisfying their bonding requirements.

II. Miscibility in the Soda–Silica System

Soda and silica are miscible in all proportions. From X-ray analysis and the laws of structural silicate chemistry, a picture of the atomic arrangement in soda-silica glass has been developed[1] which is shown in Fig. 1. Each silicon atom is tetrahedrally bonded to four oxygen atoms. The total oxygen content, including the part introduced by the soda as well as that from the

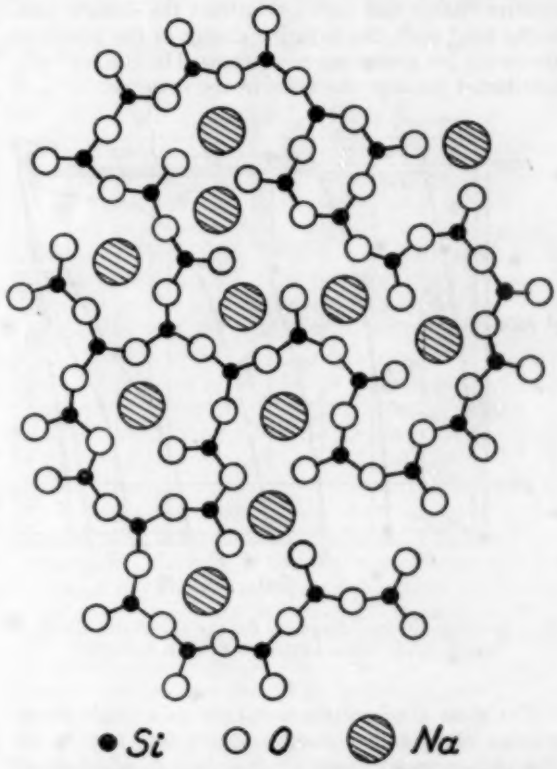

Fig. 1.—Schematic representation in two dimensions of the structure of soda-silica glass. To correspond to two dimensions, the silicons are shown bonded to three oxygens rather than to four. Each silicon atom is tetrahedrally bonded to four oxygen atoms, the fourth being directly above or below the silicon atom and therefore not shown.

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† Dr. Warren, Dept. of Physics, Massachusetts Institute of Technology; Dr. Pincus, Research Div., American Optical Company.

[1] B. E. Warren and J. Biscoe, "Fourier Analysis of X-Ray Patterns of Soda-Silica Glass," *Jour. Amer. Ceram. Soc.*, **21** [7] 259–65 (1938).

silica, takes part in the formation of the random silicon-oxygen network. As the oxygen-silicon ratio is greater than 2, part of the oxygens will be bonded to two silicons and part only to one silicon. The sodium exists as the ion Na^+ and is situated in the holes in the silicon-oxygen network.

In a qualitative way, when SiO_2 and Na_2O are fused together, the process of solution may be followed. In the silica particles, each of the oxygens is bonded to two silicons. Here and there on the surface of a silica particle, a silicon-oxygen bond will break under thermal agitation. The oxygen remains bonded to one silicon but is free from the other. Instead of the second silicon rebonding to its original oxygen, it may be easier to join to one of the extra $O^=$ ions present in the melt because of the Na_2O. Each time this process takes place, a permanent break is produced in the continuous silicon-oxygen bonding. With more and more of these breaks, the surface of the silica particle weakens, and bits of the surface break off into the melt. Because the silicon-oxygen groups break off by having combined with negative oxygen ions, they carry a negative charge and therefore attract the sodium ions. In the final melt, the negative charge of the transient silicon-oxygen groupings is neutralized by the Na^+ ions distributed through the holes in the network.

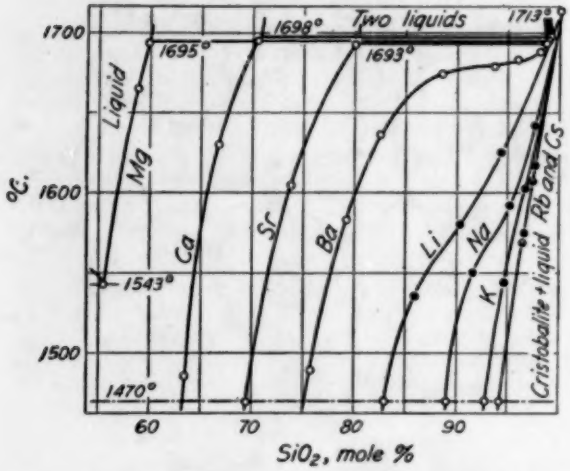

FIG. 2.—Equilibrium diagrams for the alkali and alkaline earth oxide–silica systems (F. C. Kracek[2]).

Why does a soda-silica melt exist as a single homogeneous phase rather than segregate into two immiscible phases, such as a silica-rich and a soda-silica phase? Each silicon in the melt is striving to keep itself continually bonded to four oxygens in spite of occasional breaking of bonds by the thermal agitation. This is more easily accomplished with a single phase for the soda-silica melt because the number of oxygens per silicon is higher and it is not necessary for every oxygen to be bonded between two silicons in order that each silicon shall be bonded to four oxygens.

Working in the other direction is the desire for each sodium ion to have a proper surrounding of oxygens. The oxygens, bonded only to one silicon, are the only unsaturated oxygens, and the Na^+ ions will try to surround themselves by these unsaturated oxygens. With low soda content, the number of Na^+ ions and unsaturated oxygens is small, and if they are uniformly distributed throughout the glass, they will be widely separated. It would be easier for each Na^+ ion to be in contact with several unsaturated oxygens if a phase of higher soda content were to segregate. In a soda-silica melt with low soda content, therefore, are two opposing tendencies. The continual bonding and rebonding of the silicon with all available oxygen in the melt tends to hold all of the oxygen in a single phase, whereas the attraction between Na^+ ions and unsaturated oxygens tends to segregate a phase of higher soda content. Because the sodium ion is monovalent and the sodium-oxygen bond is rather weak, the second tendency is relatively weak. The first effect predominates, and soda and silica, accordingly, are completely miscible.

III. Solubility of Alkali and Alkaline-Earth Oxides in Silica

In a lime-silica melt, there is immiscibility for low lime content. As the Ca^{++} ion is divalent, the Ca-O bond is appreciably stronger than the Na-O bond. The affinity of the silicon for all the available oxygen of the melt is outweighed in this case by the desire for the Ca^{++} ion to be properly surrounded by unsaturated oxygens. The experimental facts for a series of alkali and alkaline-earth oxides with silica are summed up by Kracek[2] in Fig. 2. The importance of the bond between oxygen and the alkali or alkaline-earth atom is greater the larger the valence and the smaller the cation. It is interesting to notice here that the curves in Fig. 2 are in the same order as the quantity, z/R, wherein z and R are the cation valence and radius. The values are given in Table I. Although the relation is only of qualitative significance, it does suggest that the greater the bond strength of the oxygen to the alkali or alkaline-earth atom, the more important it is that the cation be properly surrounded by unsaturated oxygens and the greater is the tendency for the melt to segregate into two phases.

TABLE I

RATIO OF CATION VALENCE TO RADIUS

	R	z	z/R	Type of curve
Cs	1.65 A	1	0.61	
Rb	1.49	1	0.67	Nearly straight
K	1.33	1	0.75	
Na	0.98	1	1.02	
Li	0.78	1	1.28	S-shaped
Ba	1.43	2	1.40	
Sr	1.27	2	1.57	
Ca	1.06	2	1.89	Immiscibility
Mg	0.78	2	2.56	

[2] F. C. Kracek, "Cristobalite Liquidus in Alkali Oxide–Silica Systems and Heat of Fusion of Cristobalite," *Jour. Amer. Chem. Soc.*, **52** [4] 1436–42 (1930); *Ceram. Abs.*, 9 [9] 783 (1930).

IV. Limit of Immiscibility in Lime–Silica System

The equilibrium diagram for the lime–silica system[3] is shown in Fig. 3. For a lime content of less than about 28%, the liquid segregates into two phases. With a few simple assumptions, an approximate calculation of this limiting composition may be made.

In a single-phase, lime-silica melt, there will be oxygens bonded to two silicons and oxygens bonded only to one silicon. Each Ca^{++} ion tries to surround itself by several single-bonded oxygens. Because the number of single-bonded oxygens is twice that of calcium atoms, in order that each calcium shall have a reasonable number of surrounding oxygens, it is necessary for each single-bonded oxygen to bond to more than one calcium. Two calciums bonded to the same oxygen cannot be farther apart than twice the Ca-O distance.

$$\text{Ca-Ca} = 2\text{Ca-O} = 2 \times 2.38 = 4.76\ \text{A}.$$

For a homogeneous glass with atoms uniformly distributed, the volume of glass containing one calcium atom will be of the order of magnitude of the cube of the linear separation.

$$\text{Vol./Ca} = (4.76)^3 = 108\ \text{A}^3.$$

If the composition is represented as $X\%$ by weight of CaO and $(100 - X)\%$ by weight of SiO_2, the volume of 100 grams of glass will be

$$V_{100} = \frac{100}{\rho} \times 10^{24}\ \text{A}^3.$$

The number of Ca atoms in X grams of CaO is given by

$$N_{Ca} = \frac{X}{56.1} 0.606 \times 10^{24}.$$

The volume of glass per calcium atom in A^3 is then

$$V_{Ca} = \frac{V_{100}}{N_{Ca}} = \frac{100}{\rho} \frac{56.1 \times 10^{24}}{0.606 \times 10^{24} X} = 108.$$

For the range of compositions of interest, ρ has an average value of about 2.6.

$$X = \frac{100 \times 56.1}{108 \times 0.606 \times 2.6} = 33\%.$$

In view of the approximations involved, the calculated value* of 33% is in satisfactory agreement with the experimental value of 28%. The theory of the limiting composition is purely geometrical, involving only the idea that for stability the lime content must be sufficiently high so that the Ca^{++} ions and the single-bonded oxygens are close enough together for each to have suitable surroundings. The calculated numerical value has no great accuracy or significance. The only point is that from reasonable assumptions a reasonable answer is derived, and to that extent the calculations give some insight into the factors which are important in determining miscibility and immiscibility.

The same approximations for the MgO–SiO_2 system give a limiting composition of 39% of MgO by weight as compared with the experimental value of about 31%.

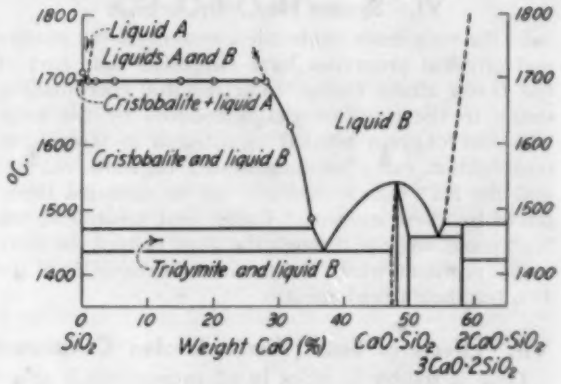

FIG. 3.—Equilibrium diagram of the system SiO_2–2CaO·SiO_2 (J. W. Greig[3]).

V. Lime–Boric Oxide System

A melt of lime-boric oxide segregates into two immiscible phases for a lime content of less than about 23% by weight.[4] In this system, there are two possibilities to be considered. For the first possibility, it is assumed that all of the boron atoms remain in triangular coordination. Owing to the extra oxygen introduced by the lime, there will be oxygens bonded to two borons and oxygens bonded only to one boron. For stability, each of these unsaturated oxygens must bond to at least two Ca^{++} ions, and following the same argument developed for the lime–silica system, a limiting composition for miscibility is calculated as 34% of CaO by weight.

The other possibility is as follows: Owing to the extra oxygen introduced by the lime, as many as possible of the borons change over to tetrahedral coordination. Each oxygen will be bonded to two borons. The four oxygens surrounding a boron in tetrahedral coordination have an unsaturated negative valence, inasmuch as a trivalent positive cation has half interest in four divalent negative ions. The Ca^{++} ions therefore try to surround themselves by oxygens which are bonded to borons in tetrahedral coordination. Each tetrahedral group must contact at least two calcium ions in order that each of the four unsaturated oxygens shall have a calcium neighbor. From the known dimensions of the group, this gives a distance of about 5.8 A between calcium atoms. The volume of glass, which on the average contains one calcium atom, will be roughly equal to the cube of the linear separation.

$$V_{Ca} = (5.8)^3 = 195\ \text{A}^3.$$

[3] J. W. Greig, "Immiscibility in Silicate Melts," *Amer. Jour. Sci.*, **13** [73] 1–44; [74] 133–54 (1927); *Ceram. Abs.*, **6** [4] 157 (1927).

* Because only the energy term of the free energy has been considered, this calculated value applies only to low temperatures; for higher temperatures, the TS term would shift the limiting composition to lower CaO values.

[4] E. T. Carlson, "System CaO–B_2O_3," *Bur. Stand. Jour. Research*, **9** [6] 825–32 (December, 1932); R.P. 510.

By using the same type of calculation, this volume per Ca atom corresponds to a composition of 19% of CaO by weight. The experimental value of 23% of CaO lies between the two calculated values of 34% and 19%. Actually the structure of the lime-borate melt is probably intermediate between the two limiting conditions which have been assumed.

VI. System Na_2O–B_2O_3–SiO_2

In the soda–boric oxide–silica system, X-ray studies and physical properties have suggested that part of the boron atoms change to tetrahedral coordination, owing to the extra oxygen introduced by the soda. The four oxygens bonded to a boron in tetrahedral coordination carry an unsaturated negative valence, and the Na^+ ions accordingly try to surround themselves by these oxygens. Under heat treatment, the Na^+ could migrate through the glass toward the more stable positions where the unsaturated oxygens of the BO_4 tetrahedra predominate.

VII. Effects of Small Amounts of a Constituent

Lime is soluble in silica in all proportions if about 1% of Na_2O or of Al_2O_3 is added. It has not been possible to develop a quantitative treatment for this problem, but in a qualitative way the explanation is fairly simple. If a small amount of soda is added to silica, the glass melt will contain unsaturated, single-bonded oxygens. When a small amount of Al_2O_3 is added to silica, the aluminum atoms probably will tend to go into tetrahedral coordination, as they do this in many silicate crystals, such as the feldspars. The Al^{+++} ion being trivalent, the four oxygens bonded to an aluminum are unsaturated. When small amounts either of Na_2O or of Al_2O_3 are added to silica, unsaturated oxygens are produced. These regions where the unbalanced negative charge exists attract the positive Ca^{++} ions. For a small lime content, the few unsaturated oxygens apparently exert enough of a stabilizing influence to hold the melt together in a single phase.

The effect seems to be solely one of adding something soluble which will produce unsaturated oxygens. If the added constituent does not produce unsaturated oxygens, the effect does not exist. If boric oxide, for example, is added to silica, the Si is in tetrahedral coordination and the B is in triangular coordination. Each oxygen is bonded to two cations (Si or B) and is saturated. Adding a small amount of B_2O_3 to silica should not have the same effect as small amounts of Na_2O or of Al_2O_3. There should be no increase in miscibility of lime in silica by adding a small amount of B_2O_3, and, experimentally, a small decrease[5] is noticed.

Ackowledgment

Many interesting points concerning immiscibility in glass systems were pointed out to the writers by W. Weyl, and it is a pleasure at this time to acknowledge these valuable suggestions.

[5] E. P. Flint and L. S. Wells, "System Lime–Boric Oxide–Silica," *Jour. Research Nat. Bur. Stand.*, **17** [5] 727–52 (1936); R.P. 941; *Ceram. Abs.*, **16** [2] 75 (1937).

POWDER METHOD FOR MEASUREMENT OF CHEMICAL DURABILITY OF GLASS*

By F. V. Tooley and C. W. Parmelee

Abstract

From the standpoint of a strictly quantitative approach to the problem of measuring the chemical durability of glass, there is need for (1) a method to measure the surface area of irregularly shaped particles that is independent of their chemical composition and surface conditions and (2) methods to measure the actual ions present in extracts from durability tests. A method of measuring (1), that is, the surface of irregularly shaped particles, has been developed, based on the principle that

$$4\,\frac{\Sigma \text{ areas of projected images of a convex particle as measured from } n \text{ random positions}}{n}$$

approaches the absolute surface area of the particle as n increases. Particles to be measured were mounted in random orientation by sprinkling them on a transparent plastic mounting medium applied in a thin film on a glass slide. After magnifying with a projection microscope and tracing the areas, the final areal measurements were made planimetrically. The procedures for measuring small concentrations of sodium and silica occurring in durability extracts were tested and were found to be applicable to the problem of measuring the extent of the attack. The procedure for determining sodium is to precipitate and weigh the triple salt, sodium zinc uranyl acetate, $(UO_2)_3\,ZnNa(CH_3COO)_9 \cdot 6H_2O$; the procedure for silica involves the production in acid solution of silicomolybdate blue by reduction of silicomolybdate yellow with sodium

* Presented at the Forty-First Annual Meeting, The American Ceramic Society, Chicago, Ill., April 19, 1939 (Glass Division). Received January 15, 1940.

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sulfite and by a photometric comparison of the color developed with a standard series. By the application of these methods in actual durability tests, it is shown that two equal volumes of the same glass collected between the same limiting screens exhibit a measured difference in surface per unit volume, which correlates closely both with chemical attack and with the positions of surface distribution curves. The evidence of this investigation corroborates the view that closer specification of the conditions under which the glass grains are prepared is desirable and that accurate determination of sodium and silica is practicable in very dilute solutions obtained in durability tests.

I. Introduction

In measuring the durability of glass by the powder method, a rate of decomposition is involved, which is expressed ultimately in terms of the amount of decomposition per unit surface per unit time. Any variation, therefore, of the method of measuring the surface attacked and the extent of the attack is important.

II. Differences in Surface Theoretically Possible

It is common practice to collect particles of glass to be used in durability tests between two limiting screens. Consideration should therefore be given to possible differences in surface per unit mass that might occur (1) in samples of the same glass prepared according to different crushing and sieving procedures and (2) in samples of different types of glasses prepared according to the same crushing and sieving procedure.

The extent to which surface differences occur between equal volumes of glass collected between the same limiting screens is indicated in Fig. 1, which shows the variation of surface per unit volume with surface per particle. For a given quantity of spherical grains collected between two limiting sieves, the total surface exposed will depend on the shape of the particles and on the distribution of sizes, that is, a given weight of larger particles will exhibit a smaller surface than the same weight of smaller particles. The variation of surface per unit volume, even between narrow limits of surface per particle, may amount to a considerable quantity, and the possibility of extremely large differences, owing to differences in distribution of particle size, increases to the left of the curve. The theoretically possible changes in surface per unit volume for spherical particles between the limits of diameter set by sieves Nos. 40 and 50 (0.417-mm. and 0.295-mm. mesh, respectively), which are commonly used to collect the grains for durability tests, are indicated by dotted lines. A further indication of surface variation theoretically possible for spherical grains within these limits is shown in Table I, which gives the percentage of deviation from the mean surface, based on the mean diameter, for 1 cc. of glass grains for fractions between the mesh limits of 0.295 and 0.417 mm. The total volume in each fraction is assumed to consist entirely of spheres of the same diameter as indicated. A shift in the distribution curve could amount to a considerable variation in the surface per unit volume. Calculations on the basis of two arbitrarily chosen distributions which might reasonably be expected to occur yield significant differences in surface per unit volume of glass. Figure 2, for example, shows two samples, *A* and *B*, in which the distributions are expressed in terms of the percentage by the number of particles of a given surface. The total surface and volume are indicated for 100 particles in each case; the total surface per 100 particles for sample *A* is larger than sample *B*. The total volume in sample *A*, however, is also larger. By converting to an equal volume basis, the surface per unit volume in sample *B* exceeds that of sample *A* by 0.82 sq. mm., an increase of 5.1% in surface per unit volume, with a shift of the distribution curve from *A* to *B*. The experiments, however, actually do not involve idealized shapes of particles but a wide variety of shapes and sizes. The range of surface per particle, moreover, exhibited by particles of crushed glass collected between two given screens will usually be larger than that exhibited if the particles are spherical and would seem to offer the possibility of even larger differences in total surface per unit volume. The duplication of distribution thus emerges as a possible experimental criterion for the duplication of surface per unit volume for samples collected between the same limiting screens.

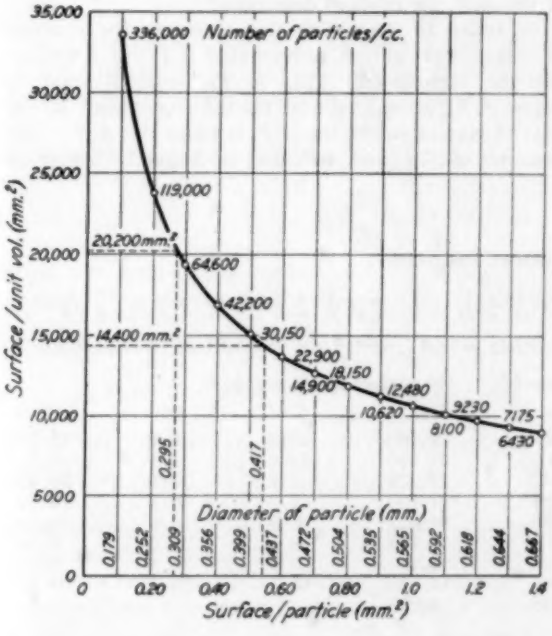

FIG. 1.—Variation of surface per unit volume of glass with surface per particle; unit volume = 1 cm.³

III. Measurement of Surface of Irregularly Shaped Particles

In vew of such theoretically possible errors in surface, some method is needed for the direct measurement of the surface of irregularly shaped particles. Such a method, to be applicable to glasses of different types, should be independent not only of the shapes of the particles but also of their chemical composition and surface conditions. The method developed by the writers requires considerable time to apply, but it seems to be more free from assumption in principle than any method yet devised for measuring the surface of irregularly shaped particles, which from sample to sample may exhibit different chemical composition and surface conditions.

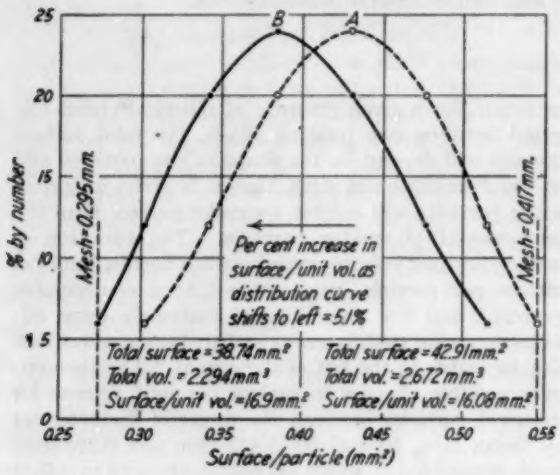
B
A
Mesh=0.295mm.
Mesh=0.417mm.
Per cent increase in surface/unit vol. as distribution curve shifts to left = 5.1%
Total surface = 38.74 mm.²
Total vol. = 2.294 mm.³
Surface/unit vol. = 16.9 mm.²
Total surface = 42.91 mm.²
Total vol. = 2.672 mm.³
Surface/unit vol. = 16.08 mm.²
% by number
Surface/particle (mm.²)

FIG. 2.

It can be demonstrated mathematically that the total surface area of a particle of convex surface, regardless of its shape, is equal to four times the average of its projected image, or the value of

$$4\,\frac{\sum \text{areas of projected images measured from } n \text{ random positions about the particle}}{n}$$

approaches the absolute surface of the particle as n increases.

To calculate the total surface area of a given amount of granular material, each grain will have a visually apparent area, hereafter abbreviated, *A.A.* when viewed from infinitely far off in a given direction. If the surface of the grain be divided into infinitesimal elements of area, dS, with normal parallel to ON, then the *A.A.*, viewed from the direction OP, is $\int |\cos \angle PON| dS$, where $|\cos \angle PON|$ means the absolute value of $\cos \angle PON$ and where the integration is over the region or regions of the surface which are actually in view, that is, not screened from view by other regions of the surface. Thus the *A.A.* of a spherical grain is the area of a great circle on its surface from whatever direction it is viewed, the region of integration being the forward hemisphere. The *A.A.* of a cube viewed normal to a face is the area of the face; viewed along a line joining the midpoint of opposite edges, it is $\sqrt{2}$ times the area of a face; and viewed along a cube diagonal, it is $\sqrt{3}$ times the area of a face. It may be shown that the average of the *A.A.* for random directions is $^3/_2$ times the area of a face or $^1/_4$ times the total surface area of the cube. For a sphere, the *A.A.* also is $^1/_4$ times the total surface area of the sphere. It will be shown that the average of the *A.A.* for random directions is $^1/_4$ times the surface area for any convex surface, that is, a surface met by any straight line, not in one of its plane faces, in not more than two points. Thus, for such a grain, the problem of finding the surface area reduces to the problem of finding the average of the *A.A.* for random directions.

In order to generalize this theorem, the concept of absolute projection, abbreviated *A.P.*, of a surface will be introduced. This is the integral used to define *A.A.*, integrated over the entire surface. In the case of convex solids, the *A.P.* is twice the *A.A.* The concepts of *A.A.* and *A.P.* may be applied whether or

TABLE I

SURFACE DATA ON SPHERICAL PARTICLES

Column (1) V = total vol. (mm.³); (2) a = diam. of sphere (mm.); (3) $\bar{v}$ = vol. of single particle = $\frac{\pi a^3}{6}$ (mm.³); (4) N = total No. of particles $\frac{V}{\bar{v}}$; (5) $\bar{s}$ = surface of single particle = πa^2 (mm.²); (6) S = surface of N particles = $N\bar{s}$ (mm.²); (7) deviation from mean (%)*; (8) surface decrease (%)†; (9) surface increase (%).‡

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
1000	0.295	0.0134	74,700	0.273	20,400	20.8	0.0	41.7
"	0.310	0.0156	64,200	0.302	19,350	14.6	5.1	34.4
"	0.330	0.0188	53,200	0.342	18,200	7.8	10.8	26.4
"	0.350	0.0225	44,500	0.384	17,100	1.3	16.2	18.8
"	0.370	0.0265	37,800	0.430	16,220	3.9	20.6	12.6
"	0.390	0.0310	32,300	0.477	15,400	8.8	24.5	6.9
"	0.405	0.0348	28,700	0.515	14,800	12.3	27.4	2.8
"	0.417	0.0380	26,400	0.546	14,400	14.7	29.4	0.0
"	0.356	0.0236	42,400	0.398	16,880			

* Calculated from surface equivalent to mean diameter a_m = 0.356 mm.
† Based on max. surface = 20,400 mm.²
‡ Based on min. surface = 14,400 mm.²

not the surface encloses a solid. For example, for a hemisphere (the plane base not being counted) the *A.P.* is $^1/_2$ the surface area for any direction, but the *A.A.* from the direction, *OP*, is the latter multiplied by $^1/_2 + {}^1/_2|\cos \angle PON|$, where *ON* is normal to the base of the hemisphere. The difference between *A.P.* and *A.A.* is that in the former all portions of the surface contribute whereas in the latter those regions screened from view do not contribute.

Random directions of a line *OP* about a fixed point *O* must now be defined. Let *C* be a fixed sphere with center at *O* and with total surface area at S_0 and let *P* be the point of intersection of the line *OP* with *C*. Then the directions of *OP* are random, if the probability of *P* lying within any region of area, *S*, on the sphere *C* is S/S_0.

The theorem which includes that stated in the first paragraph is that the average of the *A.P.* of a surface, for random directions, is $^1/_2$ the area of the surface. This is proved first for a plane region of area, *A*, containing the point, *O*, and with *OZ* normal to the plane. The *A.P.* from a direction *OP* is $A' = A|\cos \angle POZ|$. For random directions of *OP*, the probability of *P* lying within an infinitesimal region of area, *dS*, of the sphere, *C*, is dS/S_0. Hence the average of the *A.P.* for random directions is $A'_{av.} = \int A|\cos \angle POZ|\frac{dS}{S_0}$, where the integration is over the entire surface of the sphere, *C*. Now

$$A'_{av.} = \frac{A}{S_0}\int |\cos \angle POZ|\, dS = \frac{AS'_0}{S_0}$$

where S_0 is the *A.P.* of sphere *C*, for direction, *OZ*.

Since $S'_0 = {}^1/_2 S_0$,

$$A'_{av.} = {}^1/_2 A,$$

proving the stated theorem in this special case. Next, suppose that the surface is composed of *n* plane regions of area a_i with normals parallel to ON_i. Then

$$A'_{av.} = \sum_{i=1}^{n} \int a_i\, |\cos \angle PON_i|\, \frac{dS}{S_0} = \sum_{i=1}^{n} {}^1/_2 a_i = {}^1/_2 \sum_{i=1}^{n} a_i = {}^1/_2 A,$$

where A = total area of surface.

For any surface, divided into infinitesimal regions of area, *dA*, with normal parallel to *ON*,

$$A'_{av.} = \int\int dA\, |\cos \angle PON|\, \frac{dS}{S_0}.$$

Integrating first with respect to *dS* over the sphere, *C*,

$$A'_{av.} = \int {}^1/_2 dA = {}^1/_2 A.$$

The theorem stated thus has been proved in general.[1]

This principle was applied by sprinkling glass particles on to a thin film of a transparent plastic medium on a glass slide so that the particles were caught and retained in their various orientations. By the use of a projecting microscope, the areas exhibited by a definite number of particles were projected with suitable magnification on to a large sheet of tracing vellum (mounted on a glass plate) and were traced, and these areas were measured with a planimeter. From these data, together with data on the number of particles per unit volume of glass (determined by counting out and weighing a definite number of particles), a figure was calculated representing the surface per unit volume of glass grains. The type of mounting medium used was important because the application of the principle by the procedure used depends on finding a suitable transparent and plastic substance. A gel-like mixture of gum arabic, glycerine, and water and known as "Farrant's" medium was found to serve the purpose. A thin film of this material on a glass slide in contact with air for a minute or so becomes plastic while retaining softness, and the sprinkled particles are caught and held firmly in the position in which they strike the film. A suitable state of plasticity and softness was determined in practice by viewing the fresh film under a low-power binocular microscope and by scratching through the film with a wire every few seconds. The troughs at first filled in immediately; but they gradually tended to persist, until finally, usually after a minute and a fraction, there was no tendency to fill in. Particles sprinkled on at this point were caught and held in their various orientations. Before this state of plastic softness is reached and after they are caught, the particles are not held in a stationary position but tend to take a stable position. If too much time is allowed to elapse after the test indicates a proper film condition, the film becomes too hard, and the particles bounce off. With the proper precautions, however, there is no difficulty in catching and holding the grains in a stationary position.

IV. Measurement of Extent of Attack in Durability Tests

Concerning the question of the nature and manner of measuring the extent of attack in durability tests, the point of view is taken that, if interpretations of differences in durability as measured by various tests on different types of glass are to be made on a sound quantitative basis, measurements must be made, not of mass effects of a composite of causes, but of the actual amounts of the various ions taken from the glass as a result of attack by the reagent. The choice and testing of methods to determine all of the ions appearing in extracts from durability tests on various types of glass is a problem that undoubtedly will require a great deal of time and effort; but until the nature and amount of ions taken from a glass under specified conditions are known, the differences in durability cannot be interpreted on a quantitative basis in the strict sense of the term.

A differentiation must be made in this connection between two broad purposes of durability testing. If the interest is a matter (1) of control, that is, whether or not the durability standard of a given glass in production is being maintained, (2) of determining the degree of concordance between certain measurements

[1] V. A. Hoersch, Dept. of Mathematics, Univ. of Illinois, Urbana, Ill. (unpublished work).

and the actual behavior of a glass under service conditions, or (3) of detecting relatively large differences in durability, then the measurement of certain composite effects may prove to be sufficient for the purpose. If, on the other hand, information is needed to interpret satisfactorily the durability differences between glasses of widely different types on a strictly quantitative basis and to detect small differences in durability, the use of the measurements of composite effects may not offer an adequate criterion.

With this point of view, procedures have been tested and applied for the determination of sodium and silica, the two substances which, for most common glasses, would yield the most information on durability.

(1) Determination of Sodium

The method tested for the determination of sodium was that originally proposed by Barber and Kolthoff,[2] involving precipitation of the triple salt, sodium zinc uranyl acetate, $(UO_2)_3ZnNa(CH_3COO)_9 \cdot 6H_2O$, by interaction of the sodium ion with a highly concentrated solution of zinc uranyl acetate. The precipitate contains but 1.5% of sodium; in the precipitation of small amounts of sodium, therefore, a comparatively large and conveniently weighable precipitate is obtained. The precipitation is carried out by observing a ratio of not less than 10:1 of reagent to a solution that contains not more than 8 mg. of sodium; under these conditions, the triple salt is insoluble in the reagent, the latter being saturated with the triple salt because of the sodium content of the chemicals used in its preparation. The precipitation is a time reaction, and Barber and Kolthoff regard a minimum reaction time of $^1/_2$ hour sufficient to give good results. The data of Bray[3] indicate that longer periods of reaction are to be preferred, whereas Koenig[4] has obtained good results with a 15-minute digestion period.

It was convenient in the present experiments to allow the precipitation to stand overnight before filtration, and excellent results were obtained. The salt came down in large crystals and was filtered by suction through Gooch crucibles with a maximum of 10 cc. of ethyl alcohol to wash it free of excess reagent. The alcohol was removed by an ether wash, and air was drawn through the filter cake to remove the ether. After coming to equilibrium with atmospheric conditions, the precipitate was weighed. The influence of various ions on the determination are reported by Barber and Kolthoff as follows:

When the KCl content exceeds 50 mg. per cc. of solution, discordant results will follow. For every 50 mg. of KCl per cc. of solution, 10 cc. of the reagent should be added. If a large amount of potassium is present as sulfate, the method does not give as good results as when the potassium is present as chloride; K_2SO_4 is precipitated by the reagent. As barium does not interfere with the sodium determination, the sulfate ion can be easily removed as barium sulfate. Even large amounts of ammonium salts do not interfere. Strontium gives high results; a white precipitate, probably strontium acetate, appears. Barium, calcium, and magnesium do not interfere. The reagent contains usually a little sulfate as impurity; therefore, if barium is present, a little barium salt should be added to the reagent so that the sulfate ions are removed as barium sulfate; otherwise, too high results will be obtained. Zinc does not interfere. As concerns the effect of anions, it is reported that phosphate ion interferes. It is suggested that probably this ion can be removed in this form with the reagent before the sodium is precipitated. Large amounts of organic acids, such as oxalic and tartaric, interfere.

Koenig more recently has made an excellent study of the optimum conditions for the successful application of the method.[4]

(2) Determination of Silica

The method tested for the determination of silica was a photometric modification of a colorimetric method originally proposed by Isaacs[5] for determining silica in biological tissues. The chief feature of this method is the reduction of yellow silicomolybdate (previously obtained by the interaction of silica and ammonium molybdate in acid solution) by sodium sulfite; this reaction yields a blue color, the intensity of which under suitably controlled conditions is proportional to the concentration of the silica present. The silica is determined by a photometric comparison of the color developed in unknowns with that in a standard series of solutions, simulating the solution conditions of the unknowns.

(3) Application of Methods to Synthetic Solutions

Each of the methods for sodium and silica was subjected separately to preliminary studies on synthetic solutions under various conditions, and satisfactory results were obtained. Table II shows the results of the joint application of the methods to synthetic solutions prepared to simulate extracts from durability testing, that is, solutions containing ions commonly present in the extracts. Additional silica determinations were made, and the results combined with those in Table II are shown in Table III. In such solutions, the silica generally may be determined in the range of 0 to 0.36 mg., with a maximum difference of about 0.04

[2] H. H. Barber and I. M. Kolthoff, "Specific Reagent for Rapid Gravimetric Determination of Sodium," *Jour. Amer. Chem. Soc.*, **50** [6] 1625–31 (1928).

[3] R. H. Bray, "Qualitative and Quantitative Determination of Replaceable Sodium in Alkali and Nonalkali Soils," *Jour. Amer. Soc. Agron.*, **20** [11] 1160–66 (1928).

[4] E. W. Koenig, "Direct Determination of Sodium Oxide in Feldspar," *Jour. Amer. Ceram. Soc.*, **22** [1] 24–31 (1939).

[5] (*a*) L. Isaacs, "Micromethod for Determination of Silicon," *Bull. soc. chim. biol.*, **6**, 157–68 (1924).

(*b*) J. H. Yoe, Photometric Chemical Analysis: Vol. I, Colorimetry, p. 366. John Wiley & Sons, Inc., New York, N. Y., 1928; *Ceram. Abs.*, **7** [10] 726 (1928).

(*c*) J. H. Fougler, "Colorimetric Estimation of Silicon in Tissues by Isaacs' Method," *Jour. Amer. Chem. Soc.*, **49**, 429–35 (1927).

(*d*) L. A. Thayer, "Colorimetric Determination of Silica in Presence of Phosphates and Iron," *Ind. Eng. Chem., Anal. Ed.*, **2**, 276–83 (1930); *Ceram. Abs.*, **10** [2] 147 (1931).

TABLE II

DETERMINATION OF SODIUM AND SILICA IN SYNTHETIC SOLUTIONS

Test No.	Na_2SiO_3 solution (cc.)	0.4 *N* H_2SO_4 (cc.)	Composite solution† (cc.)	Sodium (gm.) Present	Sodium (gm.) Found	Silica (gm.) Present	Silica (gm.) Found
158	(L)* 1.0	2.5	0.0	0.00034		0.00007	0.00009
159	"	"	4.0	"		"	0.000098
160	"	"	10.0	"		"	0.000069
161	"	"	0.0	"	0.000333	"	
162	"	"	4.0	"	0.000382	"	
163	"	"	10.0	"	0.000340	"	
164	(M)* 1.0	"	0.0	0.0034		0.00016	0.000172
165	"	"	4.0	"		"	0.000178
166	"	"	10.0	"		"	0.000204
167	"	"	0.0	"	0.00338	"	
168	"	"	4.0	"	0.00340	"	
169	"	"	10.0	"	0.00342	"	
170	(N)* 1.0	"	0.0	0.0068		0.00036	0.000320
171	"	"	4.0	"		"	0.000334
172	"	"	10.0	"		"	0.000324
173	"	"	0.0	"	0.00679	"	
174	"	"	4.0	"	0.00678	"	
175	"	"	10.0	"	0.00675	"	

* (L), (M), and (N) represent three separate fusions of Bureau of Standards sodium oxalate and silica.
† 10 cc. of composite solution contained 0.00134 gm. of $Al_2(SO_4)_3$, 0.00150 gm. of $Fe_2(SO_4)_3$, 0.00374 gm. of $CaSO_4$, and 0.00692 gm. of $MgSO_4$.

mg. in any single determination. The photometric equipment used in these tests was constructed originally for another purpose and imposed certain conditions that would not occur with the use of a good type of commercial analytical photometer. With the latter instrument, the accuracy of the silicomolybdate blue method may be increased still further. The possibility of determining even smaller concentrations of silica was examined. By increasing the absorption cell length considerably, a satisfactory calibration curve may be obtained down to concentrations as low as 0.004 mg. of silica; in this region, the chemical resistance of Pyrex-brand test tubes in which the calibration solutions were prepared set a lower limit to the sensitivity of the method. The fact that such low concentrations are measurable is valuable because it provides a convenient means to follow the course of a reaction by the determination of silica on very small aliquots taken from the extract at different intervals during the test. The same procedure, incidentally, could probably be followed in determining sodium, gravimetrically over a part of the range of concentration and (using procedures that have been reported in the literature, based on the determination of uranium in sodium zinc uranyl acetate precipitate) colorimetrically in the lower region of concentration,[6] wherein the precipitate would be difficult to weigh.

TABLE III

RESULTS OF SILICA DETERMINATIONS BY THE SILICOMOLYBDATE-BLUE METHOD ON SOLUTIONS SIMULATING EXTRACTS FROM DURABILITY TESTS*

	SiO_2 taken (mg.)	SiO_2 found (mg.)	Difference (mg.)
L†	0.056	0.064	0.008
	0.105	0.132	0.027
	0.189	0.229	0.040
M†	0.049	0.040	0.009
	0.082	0.082	0.000
	0.148	0.165	0.017
N†	0.037	0.013	0.024
	0.073	0.062	0.011
	0.146	0.122	0.024
L‡	0.070	0.090	0.020
	0.070	0.098	0.028
	0.070	0.069	0.001
M‡	0.160	0.172	0.012
	0.160	0.178	0.018
	0.160	0.204	0.044
N‡	0.360	0.320	0.040
	0.360	0.334	0.026
	0.360	0.324	0.036

* Silica in unknowns and standards from independent sources; silica content of "unknown" solutions determined gravimetrically on large aliquots by triple dehydration with HCl.
† Three separate fusions of sodium oxalate and silica; composite solution added before determination: none to 1st member of each series, 4 cc. to 2nd member, and 10 cc. to 3rd member.
‡ Composite solution added to each member is approximately 4 cc.; 4.0 cc. of composite solution contained $Al_2(SO_4)_3$, $Fe_2(SO_4)_3$, $CaSO_4$, and $MgSO_4$ in concentrations approximating their amounts in typical extracts from soda-lime glasses by The American Ceramic Society tentative method No. 1.

V. Surface Measurements, Results and Correlation of Surface with Chemical Attack in Actual Durability Tests

(1) Experimental Conditions

The results given in Table IV were obtained by applying the foregoing methods for the measurements of surface, sodium, and silica in an actual dur-

[6] K. L. Malyarov and T. Yudenich, "Colorimetric Determination of Small Quantities of Sodium," *Zavodskaya Lab.*, **3**, 904–906 (1934); *Ceram. Abs.*, **15** [6] 191 (1936). The method involves the solution of the triple salt in acetic acid and the colorimetric determination of UO_2 by measuring the color produced with $K_4Fe(CN)_6$ in a small aliquot part.

ability test. The procedure of The American Ceramic Society tentative method No. 1[7] was followed for the conditions under which the attack ensued. The methods of crushing used for glasses G I and G II were as follows:

(1) For C I, 90% of the original glass was crushed to pass the 20-mesh screen; 2 impacts per portion per cycle were observed; ½ minute of hand sieving followed each crushing; and the test sample was collected between the main sieves by mechanically shaking for 5 minutes.

(2) In G II, the glass was recycled through the crushing and sieving operation by observing 4 impacts per portion per cycle; the materials on the 20- and 40-mesh screens were recrushed in subsequent cycles; a 2-minute period of hand sieving on a 20-, 40-, and 50-mesh nest was employed until sufficient glass was obtained on the 50-mesh sieve for testing; and finally, to insure thorough sieving, the various fractions were returned to their respective screens for a 5-minute mechanical shaking period.

Different crushing and sieving procedures were employed to see whether or not, by such changes, differences in measured surface would occur that would be reflected in differences in chemical attack. The particular alternative procedures of crushing and sieving were suggested by a fundamental difference between the procedure indicated by The American Ceramic Society method No. 1 and that by Berger[8] in work relating to the D.G.G. method. Concerning the tentative No. 1 method of The Society, used in early cooperative researches, the manner of obtaining the 40- to 50-mesh sample is not clearly specified, but the implication is that the glass is recycled through the crushing operation only until a sufficient amount is obtained on the 50-mesh screen to carry out the test or tests.[7]

It was reported that "undoubtedly a common fault in the work was the use of too much sample on the 50-mesh sieve. The ideal amount apparently is about 11 gm., and the upper limit is about 25 gm. Cooperator 21, for example, obtained an average value of 0.067 when the 40- to 50-mesh portion weighed 20 to 25 gm. and 0.073, when it weighed 45 gm." The glass is crushed for the tests (according to this report) by the following procedure:

> Crush three or four 30- to 50-gm. portions of glass by striking the pestle sharply with a hammer three or four times. Empty onto the set of sieves (20-40-50 nest). Shake by hand for 2 minutes, remove the particles on 20- and 40-mesh sieves, and recrush them as before; repeat this once again; place the nest on a Ro-Tap machine and shake for 5 minutes or shake by hand for 3 minutes, using a rotary motion following a circle of about 6 inches in diameter and making about 120 r.p.m.

In preparing D.G.G. powder, Berger[8] recommends that all (or the greater part) of the original glass be crushed to pass a preliminary screen, preferably somewhat larger than the coarser of the two main sieves. This operation is carried out by using but one (and at the most two) impact per portion of glass per crushing cycle. The material from this operation is hand-sieved for 2 minutes on the preliminary screen after which the material on the screen is recrushed, recycled,

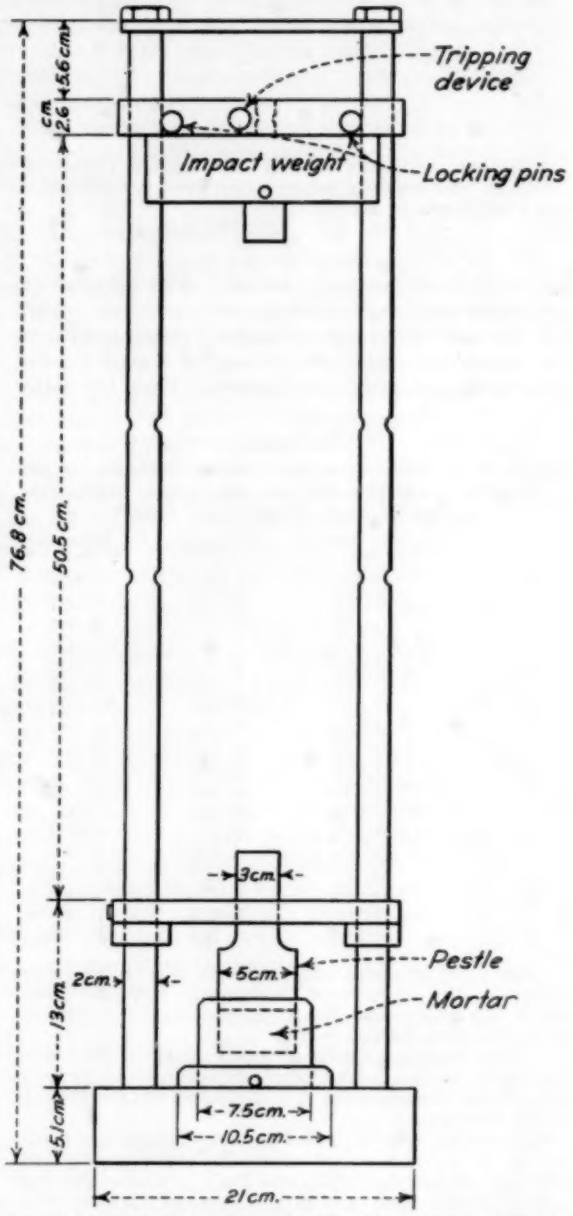

FIG. 3.—Constant impact apparatus for crushing glass for durability tests; impact weight is 5 lb. 6 oz.

[7] "Report of Committee on Chemical Durability of Glass," *Bull. Amer. Ceram. Soc.*, **14** [5] 181–84 (1935).

[8] (*a*) E. Berger, W. Geffcken, and K. v. Stösser, "Magnitude of Surface of Powdered Glass, I," *Glastech. Ber.*, **13** [9] 301–25 (1935); *Ceram. Abs.*, **15** [4] 118 (1936).

(*b*) E. Berger and W. Geffcken, "Magnitude of Surface of Glass Powders, II," *Glastech. Ber.*, **14** [12] 441–56 (1936); *Ceram. Abs.*, **18** [1] 17 (1939).

(*c*) E. Berger, "Crushing and Sieving of Glass to Ensure Control of Surface of Grains," *Jour. Soc. Glass Tech.*, **20** [81] 384–404 (1936); *Ceram. Abs.*, **17** [1] 11 (1938).

TABLE IV

SUMMARY OF RESULTS OF MEASUREMENTS OF SURFACE, Na_2O, AND SiO_2 ON SAMPLES OF GLASS PARTICLES DIFFERING IN MANNER OF PREPARATION

Column (1), glass No.; (2) limiting sieves; (3) number of particles projected, traced, and measured planimetrically*; (4) weight of glass employed in durability tests (gm.); (5) total surface = $4A_{ro}N_w$ (sq. cm.)†; (6) Na_2O by gravimetric determination by sodium-zinc uranyl-acetate method (gm.); (7) Na_2O by titration of excess H_2SO_4 (gm.); (8) SiO_2 by silicomolybdate blue photometric method (gm.).

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
G I§	40–50	720	10.0	1601 ± 0.81%	0.00668 0.00680	0.00782	0.00017
G II‖	40–50	760	10.0	1487 ± 3.77%	0.00618 0.00623	0.00763	0.00023 0.00017
G III¶	20–40	727	20.0	1678 ± 5.6%	0.00752 0.00749	0.00855	

* Four measurements employing approximately 180 particles for each.

† A_{ro} = avg. shadow area of particles in random orientation; N_w = No. particles per wt. of glass employed in tests obtained by counting and weighing particles in column (3) and calculating to wt. of glass taken.

§ Two impacts per crushing cycle per portion; 90% of original glass crushed to pass preliminary sieve No. 20.

‖ Four impacts per crushing cycle per portion; 41% of original glass passed sieve No. 20; glass recycled through crushing operation only until sufficient glass was obtained for testing.

¶ 20- to 40-sieve fraction from G I.

and resieved in the same manner until only a small amount of material remains on the preliminary screen. The glass is then sieved mechanically for 5 minutes to obtain the test sample. (In the D.G.G. method, the sample is obtained between sieves of 0.30- to 0.49-mm. mesh width.) By this procedure, it is hoped to achieve a more even volume distribution of grains.

To make possible a more quantitative expression of the crushing operation, the constant-impact apparatus (Fig. 3) was designed and constructed. By the use of this apparatus, crushing technique may be described in terms of the amount of glass in the mortar, the weight of the iron block delivering the impact, and the distance of fall. It is difficult, of course, to specify the shape of the original particles of the precrushed glass before the mortar- and pestle-crushing operation, but even here it might be desirable for the original glass to specify limits on the number of generally uniform particles per constant weight of the individual portions used in the initial crushing cycle. Berger and his associates recommended that the glass samples to be crushed "should be well-annealed, thick pieces, not of any strongly marked form."[8]

Table IV gives, for each glass preparation, in order from left to right, (3) the number of particles traced, projected, and measured planimetrically, this number representing the total of four measurements of approximately 180 particles for each; (4) the weight of glass used in the durability test; (5) the total surface area exposed, respectively, by these weights of glass, calculated from A_{ro}, the average projected image of particles in random orientation, and from N_w, the number of particles per weight of glass employed; (6) the Na_2O, determined gravimetrically on the extract by the sodium zinc uranyl acetate method; (7) the Na_2O determined by the titration method; and (8) the silica in the extract determined by the photometric silicomolybdate blue method.

(2) Discussion of Results

In the discussion of these results, because of differences between the ideal situation in applying the method for surface measurement (under which no assumptions whatsoever would be required) and the situation as it actually occurs, the figure representing the measured surface differs somewhat from the true surface. The degree of variance is controlled by the extent of these differences. The assumption is made first that the particles are truly convex, whereas they deviate from this condition in external form and in the minute irregularities on the surface. It is also assumed that the number of particles and the method of their mounting are sufficient to give a true statistical average of the random projected image. The measurement therefore does not represent the absolute surface area of the particles but an approximation to it, with the reasonable expectation that the value obtained will at least be close and directly related to the true surface.

Further study on this method should involve a consideration of (1) the degree of concavity exhibited by such particles; (2) the deviation from a true random orientation of the particles mounted as they are; and (3) the number of particles necessary to give a close approximation to the true statistical area. In the absence of data enabling an evaluation of these differences from the ideal condition under which the method gives a true measure of the surface area, results must be evaluated in terms of the consistency of the total picture, which involves the surface measurements, the amount of attack observed, and the surface-distribution curves of the particles.

By comparison of the total measured surface with the amount of sodium extracted, the differences occur in the proper order, namely, the largest amount of sodium was extracted where the largest surface was exposed. In a plot of surface against amount of material extracted, a straight line passing through the origin should result. Such a result is presented by these data (Fig. 4). Some interesting points are suggested here. First, G I and G II are on a straight line that intersects the origin; next, representative samples appear to be more readily obtainable from G I than from G II or G III (probably because the ratio of limiting sizes is greater for G III). In the case of G I, the greater amount of the

original glass passed through the preliminary 20-mesh screen. Too much weight is not to be given to the point representing G III because (1) there is difficulty in securing a representative sample and (2) owing to the greater quantity of glass used in the durability tests, the experimental conditions under which the attack ensued were somewhat different from those of G I and G II. The solid points refer to the estimation of sodium oxide by titration. According to the analysis of a typical extract on a similar glass,[7] it is apparent that a part of the alkali titration that is calculated to sodium oxide in reality is due to calcium oxide and to magnesium oxide. It has been estimated that about 92% of the titration represents sodium oxide. These points therefore, if corrected, would come somewhat lower but still a little higher than the sodium oxide actually determined. A direct determination of sodium oxide is generally preferable to an estimation, especially in view of the ease with which the actual determination can be performed.

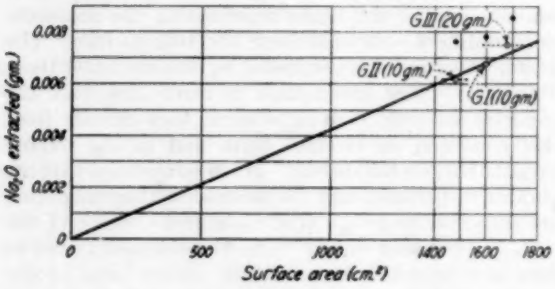

FIG. 4.—Comparison of determined surface of glass particles with Na_2O extracted by 4-hour digestion with $N/50$ H_2SO_4 at 89.5° ± 0.1.

Berger,[8] employing the same generalization for surface measurement but using a photoelectric method of measuring the shadow surfaces or random projected images, obtained a value of 800 sq. cm. per 4 cc. for D.G.G. glass grains collected between 0.3 to 0.49 mm.-mesh screens. By iodoeosin staining, a surface of 1880 sq. cm. per 4 cc. was indicated; after the fine surface roughness was removed by acid etching, iodoeosin etching gave a value of 1200 sq. cm. per 4 cc. The estimation of the surface by a comparison of relative acid attack on unknowns and measured surfaces gave values of 1130 to 1215, depending on the manner in which the glass was prepared. Berger considers his result (obtained photoelectrically on the basis of the optical shadow surface or random projected image) to be considerably low, owing to the fine roughness of surface and concavities of the grains. The values of 1480 to 1600 sq. cm. per 10 gm. ≏ 4 cc. (density = 2.5) obtained in this investigation on grains, somewhat smaller on the average (limiting mesh widths, 0.295 to 0.417 mm.) than those used by Berger, are much more in line with his values as measured by iodoeosin and by acid attack, and they are much higher than his shadow surface value which he considered to be low.*

Gross[9] obtained a value of 176.5 sq. cm. per gm. for crushed quartz (of the same size range of the grains used in this investigation) by the hydrofluoric acid dissolution method (a comparison of acid attack on measured and unknown surfaces; initial rate calibrated independently by measuring the surface by deposition of silver). This value, converted to a comparable basis, gives 1870 sq. cm. per 4 cc. It is believed therefore that Berger's results, using a photoelectric measurement of the random projected images, are too low, not altogether because of the fine roughnesses of the particles but because of some inherent defect in the method of measurement. His method involves a measurement of the difference in the amount of light reacting on two photoelectric cells, the light in one case reaching one of the cells without any interference, and, in the other case, reaching the cell after interference by the glass grains which lie loosely on a glass support fitted with a suitable diaphragm to render them opaque to the passage of light. With such an arrangement, the grains are allowed to remain stationary, and the direction of view (or light source) and the position of the cell are varied. There was a limiting maximum angle, however, through which the illuminating source could be moved and beyond which the shadows of the particles would interfere with each other. It is suggested that this difficulty, as well as the use of assumptions regarding the diaphragm to render the grains opaque are responsible for the low value obtained. A combination of the mounting technique described in this work with some photoelectric-measuring mechanism perhaps would offer an improvement in the technique of surface measurement. Such a measurement unfortunately does not give data on individual particles which allow a distribution curve to be constructed.

Finally, it is necessary to determine whether or not this correlation of surface exposed with the amount of sodium oxide removed is reflected in the distribution curves of the particles. This discussion is confined to particles of samples G I and G II, collected between the same limiting screens. Figure 5 shows such distribution curves. The distribution represented by sample G I is generally to the left of G II, and although the surface per 100 particles is smaller, the surface per 10 gm. of glass is larger owing to the greater number of particles per gram. The surface per 10 gm., as calculated from the distribution curve, serves as a convenient check on the surface figure obtained as an average of the totals of the individual readings.

VI. Summary and Recommendations

(1) A method which is independent of chemical composition and surface conditions has been developed to measure the surface of irregularly shaped particles.

(2) Methods for the gravimetric determination of

* Owing to the smaller-sized particles, some increase over Berger's value is to be expected.

[9] John Gross, "Crushing and Grinding," *U. S. Bur. Mines Bull.*, No. 402, 148 pp. (1938); p. 34; *Ceram. Abs.*, **17** [8] 286 (1938).

sodium (by precipitation and weighing of the triple sodium zinc uranyl acetate) and for the photometric determination of silica (on the basis of silicomolybdate blue) have been tested and found to be conveniently applicable to the problem of the determination of sodium and silica in extracts from durability tests. The determination of actual ions in durability extracts is to be preferred generally to that of the effects of a composite of causes.

(3) Two equal volumes of the same glass collected between the same limiting screens have been shown to exhibit measured differences in the surface which correlate closely both with chemical attack and positions of their respective distribution curves.

(4) A constant impact apparatus to make possible the expression of the crushing operation in more quantitative terms was designed, constructed, and employed.

(5) The evidence, in general, points to the conclusion that closer specification of the conditions under which the glass grains are prepared is desirable in order to obtain a more uniform distribution of particles. There is no evidence that the estimation of sodium oxide by titration is unreliable as a measure of durability differences, and the question will probably remain a moot one until the titration results can be compared in a great many cases with results of the measurements of the various ions in the solution. The view, however, is taken even *a priori* that, if convenient and accurate means were available for measuring the actual ions present, these methods would furnish data that are more easily interpretable quantitatively than would any measure of an effect of a composite of causes.

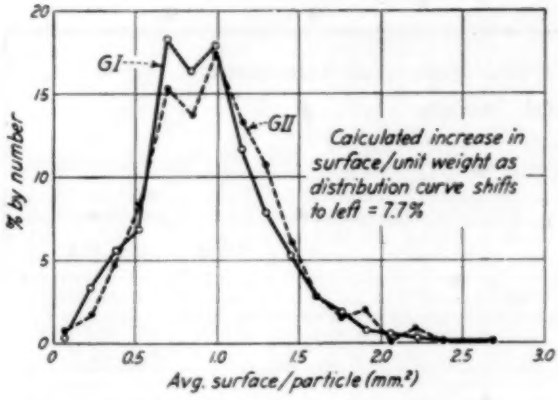

FIG. 5.

	GI	GII
No. of particles/gm.	17,200	15,200
Wt./100 particles (gm.)	0.00582	0.00658
Surface (sq. mm.)/100 particles	93.78	98.35
Surface (sq. mm.)/10 gm.	1610	1495

Concerning the future work on this problem, the following recommendations are made: (1) The ratio of limiting sizes of the grains used in durability tests should be made smaller, and the range of limiting screens employed should be shifted to the right on the curve relating surface per unit volume to surface of a single particle. Each point will serve to reduce the theoretically possible differences in surface per unit volume occasioned by differences in distribution within the range.

(2) Some of the experimental work of the Committee on the Chemical Durability of Glass should be repeated in determining sodium and silica directly by the methods described here as well as the alkali by titration. With a knowledge of the actual ions removed from various glasses tested under various known conditions, a more systematic picture of durability will be possible, in general permitting a more satisfactory basis of prediction. The determinations on sodium and silica described should be tested under conditions as they occur in extracts from a wide variety of glasses to decide what precautions are necessary in their application. Procedures applicable to all the other ions appearing in durability extracts should also be tested, such tests to lead ultimately to a set of methods for all ions appearing in extracts from durability tests on all types of commercial glasses; this would include procedures for boron, potassium, magnesium, calcium, lead, iron, and aluminum. With the recent rapid advances in applying organic reagents in the gravimetric and colorimetric determination of various elements and the advances in colorimetry and photometry, suitable methods no doubt could be found.

A few procedures worthy of investigation to determine these ions are (*a*) the picrolinic acid method for the gravimetric determination of small amounts of calcium, potassium, and lead; (*b*) quinalizarin for the formation of magnesium lakes, enabling the colorimetric determination of magnesium; and (*c*) for aluminum, several alternatives, namely, the aurintricarboxylic acid method, the "morin" fluorescent green method ($Al(C_{15}H_9O_7)_3$), and the alizarin S method are suggested. Lead may be determined colorimetrically in very low concentrations employing diphenylthiocarbazone reagent.[10] This list of possible methods is brief, but it suggests some which have been developed that might be valuable in the general problem of measuring chemical attack.

(3) A crushing and sieving procedure should be adopted, employing apparatus that will allow the procedure to be specified as nearly as possible in quantitative terms. It is recommended that a uniform constant impact apparatus of the type described be employed by all investigators in the preparation of the glass particles when the crushing is made by impact, with the following specifications: (*a*) total weight of original glass used in crushing operation; (*b*) general form and number of particles per unit weight (e.g., 40 to 50 gm.) of glass before standard mortar and pestle crushing; (*c*) average weight of mortar portion employed in each subsequent cycle of crushing and number of such portions per crushing cycle; (*d*) distance of fall of impact weight, weight of impact, and number of impacts observed per mortar portion; (*e*) number of crushing cycles observed; (*f*) weights of various fractions of glass follow-

[10] F. Feigl, "Organic Reagents in Inorganic Analysis," *Ind. Eng. Chem., Anal. Ed.*, **8**, 401–11 (1936).

ing each crushing cycle; (g) details of sieving operation (when a given quantity of glass is divided into several separate portions, this should be indicated).

(4) Work should be continued on surface measurement to develop a technique that will furnish the necessary data in a shorter amount of time. The microscopic measurement of linear intercepts of the mounted particles, using a recording stage micrometer, may be the solution to this problem.

Acknowledgments

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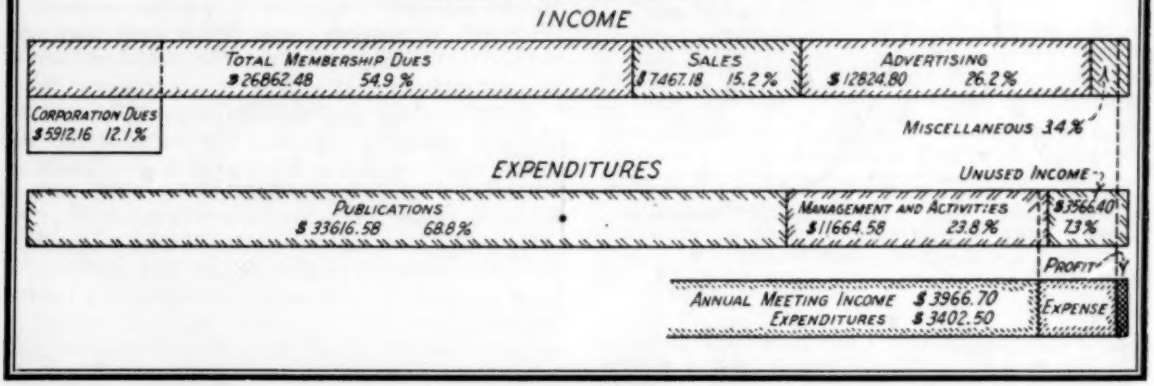

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October, 1940
19—10

Abrasives

Automatic polishing of metallurgical specimens using cast-iron and lead laps. Tracy C. Jarrett. *Trans. Amer. Soc. Metals*, **27** [3] 758–70 (1939); *Met. Abs.*, **6** [12] 517 (1939).—The recommended procedure comprises grinding with emery powders M 303 and M 305 on a cast-iron lap using kerosene as a lubricant and polishing on a lead lap using three or four grades of levigated alumina applied as a paste with purified kerosene. The laps should be run at 90 r.p.m., and the head, holding six specimens, at 200 r.p.m. in the reverse direction. The polishing time varies from 2 to 6 hr. The method is claimed to produce very flat surfaces, prevent flow of metal, and lessen the tendency for inclusions to be dragged out during polishing.

Grinding aluminum and its alloys on the wheel. Anon. *Rev. Aluminium*, **16** [109] 1624–26 (1939); *Met. Abs.*, **6** [7] 272 (1939).—Different abrasives and binders and the effect of particle size and grinding speed are discussed. Wheels suitable for various purposes are recommended.

Machinery for grinding hard metals and its importance in the workshop. Paul Feldmann. *Werkstatt & Betrieb*, **71** [19–20] 257–58 (1938); *Met. Abs.*, **6** [5] 190 (1939).—The requirements for machinery for the grinding of hard-metal tools are examined. The various stages in the process are described, and illustrated descriptions of recent types of machines are given.

Mechanism of wear. T. V. Matthew. *Jour. S. African Inst. Engrs.*, **38** [7] 229–58 (1940); abstracted in *Bull. Brit. Non-Ferrous Metals Research Assn.*, No. 130, p. 100 (1940).—The causes and mechanism of wear and tests of relative wear are summarized together with notes on the application of wear theory to recent developments in engineering practice. Numerous metals and alloys are mentioned.

Structure of polished metallic surfaces. P. A. Jacquet. *Tech. Moderne*, **31** [12] 427–37 (1939); *Met. Abs.*, **6** [9] 359 (1939).—J. describes the technique of polishing by using files, emery papers, polishing cloths, and powders. The study of polished surfaces is divided into 4 periods: (1) before 1900, empirical; (2) 1900 to 1926, introduction of scientific method and the metallurgical microscope; (3) 1927 to 1933, use of electron diffraction and (4) 1934 to 1939, electrolytic polishing. The optical and electrochemical properties of polished metals and, in particular, the properties of thick deposits of copper on cleaned and on polished copper cathodes are described.

Surface finish. G. Schlesinger. *Jour. Inst. Production Engrs.*, **19** [3] 87–111 (1940); *Machinery* [London], **55** [1433] 721–29 (1940); abstracted in *Bull. Brit. Non-Ferrous Metals Research Assn.*, No. 131, p. 137 (1940).—S. gives a preliminary report, from the Research Department of the Institution, of a research dealing with the definition of surface finish, units of measurement, symbols for use on drawings, and a comparison of methods of observation. Various methods of finishing are discussed (boring, grinding, turning, honing, lapping, and superfinishing) together with instruments for measuring surface finish, both optical and touch types (Profilometer and Contorograph).

Variables of polishing. W. E. Warner. *Machinist* [European Edition], **82** [38] 518E (1938); *Met. Abs.*, **6** [1] 25 (1939).—A wheel speed of about 7500 ft. per min. is usually adopted for polishing, and this should be kept constant; vibration must be reduced as far as possible.

PATENTS

Abrasive metal carbide manufacture. R. R. Ridgway (Norton Co.). Can. 388,692, May 14, 1940 (Aug. 10, 1939; in U. S. Nov. 21, 1935). G.M.H.

Abrasive and process of producing. J. H. Berger (American Cyanamid Co.). U. S. 2,209,292, July 23, 1940 (Sept. 13, 1939).—Abrasive grit is wetted with a solvent for an aminotriazine-aldehyde resin and bonded with a resin containing an aminotriazine-aldehyde condensation product.

Buffing wheel. C. J. Peterson and A. H. Peterson. U. S. 2,209,089, July 23, 1940 (June 14, 1938).

Centerless bar grinder machine. G. W. Binns and B. A. Kearns (Cincinnati Grinders, Inc.). U. S. 2,211,685, Aug. 13, 1940 (April 6, 1939).

Centerless grinding machine. J. E. Bergström. U. S. 2,210,137, Aug. 6, 1940 (Aug. 4, 1937).

Cleaning abrasive sheet material. G. H. Orfald. U. S. 2,210,728, Aug. 6, 1940 (Aug. 16, 1937).

Crankshaft grinding machine. J. I. Garside and C. G. Flygare (Norton Co.). Can. 389,485, June 18, 1940 (March 24, 1938; in U. S. March 26, 1937). G.M.H.

Design for grinding wheel unit. M. A. Hollengreen and R. E. Price (Landis Tool Co.). U. S. 121,789, Aug. 6, 1940 (March 29, 1940).

Furnace for making abrasive metal carbides. R. R. Ridgway (Norton Co.). Can. 388,691, May 14, 1940 (Nov. 12, 1936; in U. S. Nov. 21, 1935). G.M.H.

Grinding and lapping machine. F. J. Bullard. U. S. 2,209,071, July 23, 1940 (July 24, 1937).

Grinding wheel feeding mechanism. H. E. Balsiger and R. E. Price (Landis Tool Co.). U. S. 2,211,530, Aug. 13, 1940 (March 16, 1938).

Grinding wheel truing apparatus. C. C. Alvord (Norton Co.). Can. 389,484, June 18, 1940 (March 14, 1938; in U. S. March 15, 1937). G.M.H.

Knife-grinding machine. Andrew Ivancin. U. S. 2,211,014, Aug. 13, 1940 (Nov. 28, 1938).

Lapping machine. T. H. Nye and H. S. Indge (Norton Co.). U. S. 2,211,729, Aug. 13, 1940 (Jan. 13, 1939).

Machine for grinding. R. W. Osborn (Johnson Products, Inc.). U. S. 2,211,350, Aug. 13, 1940 (April 7, 1939).

Method and means for forming or dressing the operated surface of grinding wheels. Coventry Gauge & Tool Co., Ltd., S. J. Harley, and J. E. Wainwright. Brit. 523,164, July 17, 1940 (Dec. 23, 1938).

Method and means for forming grinding wheels for use in grinding internal screw threads. Coventry Gauge & Tool Co., Ltd., S. J. Harley, and J. E. Wainwright. Brit. 522,416, July 3, 1940 (Nov. 8, 1938).

Piston ring grinding machine. R. W. Young (Charles H. Besly & Co.). U. S. 2,209,711, July 30, 1940 (June 15, 1938).

Precoated grain abrasive article. A. G. Scutt (Carborundum Co.). Can. 388,953, May 28, 1940 (May 31, 1939). G.M.H.

Preserving coated abrasives. F. J. Crupi (Behr-Manning Corp.). U. S. 2,209,715 and 2,209,716, July 30, 1940 (Dec. 27, 1938).

Surface-finishing machine. A. H. Dall and Frank Esz (Cincinnati Grinders, Inc.). U. S. 2,209,307, July 30, 1940 (March 22, 1940).

Tap chamfering machine. Franklin Judge. U. S. 2,209,228, July 23, 1940 (Aug. 18, 1938).

Wide abrasive belt. E. P. Dahlstrom (Carborundum Co.). U. S. 2,209,074, July 23, 1940 (March 28, 1938).

Worm element lapping machine. J. C. Drader and James Martin (Michigan Tool Co.). U. S. 2,209,562, July 30, 1940 (April 15, 1936).

Art and Archeology

Analysis of the body material of ancient faience found at Antioch-on-the-Orontes. Earle R. Caley. *Tech. Studies Field Fine Arts*, **8**, 151–54 (1940); *Chem. Abs.*, **34**, 3038 (1940).—The body was white, devoid of glaze, very friable, and composed of fine grains of cemented quartz. The composition was SiO_2 98.64, CuO 0.27, R_2O_3 0.29, CaO 0.11, K_2O 0.12, Na_2O 0.08, and loss on ignition 0.55. The presence of Cu seems to support the theory that the glaze was sometimes used as a binder for quartz particles that formed the body material of ancient faiences.

Ancient stained glass in southeast Essex. F. Sydney Eden. *Connoisseur*, **105** [464] 148–52 (1940).—E. describes windows of 14th and 15th century glass in old churches in this locality. Illustrated. M.E.P.

Chinese porcelain and stoneware. Frank Davis. *Illus. London News*, **104** [2716] 842 (1939).—A Temoko porcelain bowl covered and decorated with a brown and cream glaze was excavated at Fuchow. A stoneware vase found in a grave at Wuchow near Nanchang was covered with a green glaze over black. The decoration consisted of a dragon and tiger in relief around the neck and a bird on the cover. Illustrated. L.F.M.

Chün Yao bowl. *Connoisseur*, **105** [465] 219 (1940).—Full page color illustration of a bowl of extremely fine quality (Sung dynasty). The bowl is lavender gray glazed with purple and crimson splashes. M.E.P.

Early celadon porcelain. A. L. Hetherington. *Arts & Dec.*, **51** [6] 12, 13, 47 (1940).—Celadon porcelain is distinguished by a covering of green glaze, varying from an olive green through lighter greens to a green with a distinctly bluish tone. The Chang brothers originated this glaze in the 13th century. The "Ko" ware or the "Elder Brother's" ware was well-marked by a crackle imparted to the glaze. The glaze on Sung ware contained minute bubbles and tiny particles of unmelted quartz. The younger Chang strived for a green jade effect. The decoration of celadons consisted of floral designs produced by carving or etching. Illustrated. L.F.M.

History of the manufacture of colored glass. Anon. *Glashütte*, **69** [22] 391 (1939).—Beautiful colored glass, imitation precious stones, and mosaic enamels were manufactured in Murano and Venice in the time of Marco Polo. Briani and Dominico Miotti made the first artificial garnets, agates, the colored "margaritae," etc. Giovanni of Murano made the finest stained glass for windows. Beroviero, Angelo, and Martino were the most celebrated makers of colored glass in the Republic of Venice. Toward the end of the 15th century, filigree glass and millefiori glass were invented. Colored glass manufacture reached its peak in Venice and Murano during the 16th and 17th centuries. A century later, England, France, and Germany were also making fine colored glassware. In 1680 in Potsdam, Johann Kunkel made the first gold-ruby glass. In Turnau in Bohemia the Fischer brothers made the gems called "Bohemian brilliants." With the expansion of trade, these compositions took precedence over the Venice and Murano imitations. In 1732 the green coloring chrome salts were first used in Germany, and at the end of this century, after the discovery of uranium by Martin Heinrich Klaproth, uranium glasses were first fused. In 1817 selenium was discovered by the Swedish chemist Jörns Jakob of Berzelius, and the color pallet for glasses was completed. In the middle of the 19th century the first salmon-red and selenium-ruby glasses were made, and toward the end of the century opalescent glass and marble glass in different colors were produced. The rare earths were first used to color glass in the 20th century; they gave delicate shades, and, when they were used in combination with other coloring substances, new colors were originated. See *Ceram. Abs.*, **18** [10] 267 (1939). M.V.C.

History of Saxon glass plants. Albert Schröder. *Sprechsaal*, **73** [21] 185–87 (1940).—S. gives brief historical notes on the old Saxon glass plants of the Schönecker forests, the Kottenheide and "Trützschlersche" plants, and the plants of Friedrichsgrün of the Middle Ages. The plants manufactured ordinary glassware, but they are of interest because their history gives a good picture of four centuries of glass-plant operation in one region. Besides household ware, the principal products of these plants were wine and beer glasses for bars in the town halls, apothecary jars and glassware, and glassware for the Leipsig Fairs and the banquets of graduates of Leipsig University. See *Ceram. Abs.*, **19** [5] 111 (1940). M.V.C.

Modern ceramics. Anon. *Arts & Dec.*, **51** [5] 6–7 (1940).—Modern American ceramics exhibited at the Syracuse Museum of Fine Arts are illustrated. L.F.M.

New Orrefors gallery. Helen Comstock. *Connoisseur*, **105** [464] 166 (1940).—At this gallery, a miniature theater shows films on the manufacture of glass, methods of blowing and engraving, production of "Graal"

glass in which the design is introduced between an inner and outer layer of crystal, and the newest product of the factory, "Ariel" glass, which is designed by manipulation of the air bubbles during the process of blowing. The glass of the exhibition represents such designers as Vicke Lindstrand, Sven Palmqvist, Edvin Ohrstrom, and Edvard Hald. Illustrated. M.E.P.

Old Bow porcelain in the Walters Art Gallery. ANON. *Bull. Amer. Ceram. Soc.*, **19** [8] 304–306 (1940).

Oriental acquisitions in Baltimore. HELEN COMSTOCK. *Connoisseur*, **105** [464] 166–67 (1940).—Additions to the Oriental Department of the Baltimore Museum of Arts include an important Wan Li vase. The vase is unusually tall (17¾ in.), of broad flaring outline, and is covered with a rich apple-green glaze, reserved below the lip where the *nien ko* of Wan Li appears in underglaze blue on white. There are three Han pieces, a number of Ting Yao pieces of the Sung period, and two very early examples, a Chou tripod pottery cauldron which is dark gray with deeply incised hatching and a pottery urn of the Neolithic period of a buff earthenware with a geometrical design painted in black and red. M.E.P.

Prehistoric beads of the Northern Transvaal and Natal. J. F. SCHOFIELD. *Trans. Roy. Soc. S. Africa*, **26**, 341–71.—The color and shape of the beads are described. Measurements are given in many cases. The three series of beads are believed to have come from Europe. The first series probably came from Flanders (1500) and the second from Italy (1660). V.L.B.

Pottery from the Salisbury District, Southern Rhodesia. STAPLETON AND J. F. SCHOFIELD. *Trans. Roy. Soc. S. Africa*, **26**, 321–40.—The topography of several archeological sites in Southern Rhodesia is described, and the characteristics and a proposed classification for the pottery are discussed. Illustrated. V.L.B.

Rare South Jersey glass. HELEN COMSTOCK. *Connoisseur*, **105** [465] 215 (1940).—An interesting phase of early American glassmaking was the production of noncommercial pieces, personal objects made to suit individual tastes and needs. It was customary in New Jersey, New York, and New England to take the pot metal left over in the production of window glass and bottles and to blow, for pleasure and amusement, objects in which imagination was allowed free play. The South Jersey tradition was influenced by the Belgian and Dutch workmen brought in by Caspar Wistar in 1739, but it was the English and Continental influences that finally developed the American forms found in the eastern area and in the Ohio River Valley. Illustrated. M.E.P.

John Sadler, potter and transfer printer. H. BOSWELL LANCASTER. *Connoisseur*, **105** [461] 22–27 (1940).—John Sadler became a printer and engraver in the Liverpool district in 1748, having learned the trade from his father who had learned it while a soldier in the low countries. He dreamed of decorating pottery from copperplate engravings and made many secret experiments to that end. He finally took Guy Green into partnership and perfected his method of transferring the engraving by paper from the copperplate to the ware. By this method they printed 1200 earthenware tile of different patterns in 6 hr. This was more than 100 skillful pot painters could have done in the same time. Sadler was one of the discoverers of transfer printing on pottery, and much of that done in the latter 18th century is attributed to him. Even in 1774, when Sadler had retired and Green was running the business, Wedgwood sent his creamware "in the white" to be decorated there. Illustrated. M.E.P.

Wedgwood plaques. FRANK DAVIS. *Illus. London News*, **104** [2717] 898 (1939).—A pair of Wedgwood Bentley blue and white jasper plaques of George III and Queen Charlotte was loaned to the exhibition at Luton by Queen Mary. The plaques are enclosed in their original ormolu frames. Illustrated. L.F.M.

BOOKS AND SEPARATE PUBLICATIONS

Catalogue of Italian Majolica: Vols. I and II. BERNARD RACKHAM. Victoria and Albert Museum, London. Price Vol. I 13s 3d, Vol. II 16s 9d. Reviewed in *Times Lit. Supp.*, **39** [2005] 329 (1940).—R., until lately Keeper of the Department of Ceramics in the Victoria and Albert Museum, has made a most important contribution to the recent literature of the subject. Volume I, comprising the catalogue descriptions, covers nearly 1500 entries, including the Salting Bequest. Volume II contains 222 plates illustrating almost every example catalogued. As a result of this work, many of the conclusions of R.'s earlier work have been modified. See "Guide...," *Ceram. Abs.*, **18** [10] 263 (1939). K.W.W.B.

Key to Pottery and Glass. BERNARD RACKHAM. Archibald Blackie, Winnipeg, Canada. 170 pp. 16 plates. Price 5s. Reviewed in *Times Lit. Supp.*, **39** [2005] 329 (1940).—R. deals with the pottery and porcelain of Europe and the Near and Far East from Neolithic times to the present. Glass is treated from its beginnings in Egypt before 3000 B.C. to the present. This work is intended to be an introduction to the subject, but it is so thoroughly grounded that it will be found a readable general survey by the student. K.W.W.B.

Mineralogical Investigation of Chrome-Tin Pinks as Ceramic Stains. PAUL G. HEROLD. *School Mines & Met., Univ. Missouri, Bull., Tech. Ser.*, **13** [2] 18 pp. (1939).—Stains composed of various mixtures of Cr_2O_3, $CaCO_3$, and SnO_2 were made by firing to 1335°C. and treating in the usual way. Good red colors were produced only when the mixtures were near the composition of calcium stannate and contained not more than 20% Cr_2O_3. Lavender colors were produced only when the mixtures were near the composition of pure SnO_2 and contained not more than 15% Cr_2O_3. An X-ray examination of the stains showed that the red color apparently contained only calcium stannate and that there was no increase or decrease in the molecular size which might indicate solid solution. Chemical analysis showed that the red stains contained Cr_2O_3. A microscopic examination showed that these stains were red in reflected light and colorless in transmitted light. This effect is common with colloidal materials suspended in liquids or solids and is known as the Tyndall effect. The red color of chrome-tin pink stains is apparently due to the dispersion of fine grained Cr_2O_3 on calcium stannate. From the laws of colloidal chemistry it is deduced that fine sols cause a red reflected color of medium intensity and, as the grain size of the sol is increased, the color passes from orange to yellow with an increase in intensity. With even coarser grains, the color passes from yellow through green to blue with a slight decrease in intensity. This being true, the calcium stannate then has the power to stabilize Cr_2O_3 to a small grain size while the tin oxide stabilizes the Cr_2O_3 to a much coarser particle size. P.G.H.

Potter's Book. BERNARD LEACH. Faber and Faber, Ltd., London, 1940. 159 illustrations, 4 color plates. Price 21s.—L., a practical potter, has worked both in the Far East and in England. The book, which is intended mainly for the guidance of the craftsman-potter, provides a large quantity of technical information which should render it of the highest educational value. Four types of pottery, Japanese raku, English slipware, stoneware, and Oriental porcelain, are dealt with. L. shows how to apply to pottery standards similar to those which hold good for other forms of art. Form, pattern, and brushwork are traced to their origin in human need and character and shown to be conditioned by the natural qualities of raw material. The student of pottery learns how to adapt recipes of pigments and glazes and designs of kilns to local conditions. A vivid workshop picture is given of the making of a kiln load of pots, stage by stage and problem by problem, from start to finish. The position of the individual or artist-potter in an industrial age is discussed. K.W.W.B.

Pottery; Its Craftsmanship and Its Appreciation. EDMUND DEFOREST CURTIS. Harper & Bros., New York, 1940. 100 pp., 19 illustrations. Price $2.—C., who has spent his life studying and perfecting methods and techniques for producing fine American ware, considers ceramics as a means of artistic expression. The book is intended for both the serious student of ceramics interested

in historical trends, artistic merit, and appreciation and the craftsman eager to perfect methods, formulas, and techniques. The different types of clay, methods of preparation for various purposes, and the forming, drying, glazing, and firing of useful clay products are discussed. Latest techniques are given for working with clay, either as a hobby or professionally, from the viewpoint of making products that are useful, durable, and artistically designed. Formulas for making various glazes and complete instructions for making earthenware, stoneware, porcelain, and other types of clay products are included. The book tells how to judge superior products, how to look at museum pieces, the historical importance of pottery down through the ages, the influence of ancient craftsmen on those of today, etc.

Wedgwood Club's Review for 1939. ANON. Wedgwood Club, Wellesley Hills, Mass. Reviewed in *Connoisseur*, **105** [461] 32–33 (1940).—Various copies of the Portland vase, including Wedgwood's, and of some Wellington pitchers (not Wedgwood but of interest to the members of the club) are described. Illustrated. M.E.P.

PATENTS

Decorating machine. R. S. DAVIS (Solar Laboratories). U. S. 2,209,688, July 30, 1940 (Feb. 1, 1936).

Designs for:

Bottle. S. P. BENJAMIN, JR. (Cosmetics Research Corp.). U. S. 121,802, Aug. 6, 1940 (Dec. 28, 1939). W. R. LEACH (Carr-Lowrey Glass Co.). U. S. 121,959, Aug. 13, 1940 (May 3, 1940).

Bowl. E. W. FUERST (Libbey Glass Co.). U. S. 121,588, July 23, 1940 (Jan. 26, 1940).

Chinaware, earthenware, porcelain, etc. NERLICH & Co. Can. 12,756, May 21, 1940. G.M.H.

Drinking cup. G. B. COOKE (Crown Cork & Seal Co., Inc.). U. S. 121,805, Aug. 6, 1940 (May 29, 1940).

Flashlight lens. EDWARD KATZINGER CO. Can. 12,788, June 10, 1940. G.M.H.

Hurricane lamp. A. J. BENNETT. U. S. 121,759, Aug. 6, 1940 (Feb. 6, 1940).

Jelly tumbler. W. J. LUNDY (Olean Glass Co.). U. S. 121,573, July 23, 1940 (May 23, 1940).

Plate. OTTO BAR (Bailey-Walker China Co.). U. S. 121,862 to 121,864, Aug. 13, 1940 (June 22, 1940). MARCELLINE GOUGLER (Mayer China Co.). U. S. 121,809 and 121,810, Aug. 6, 1940 (June 1, 1940).

Tile. LURELLE GUILD (Corning Glass Works). U. S. 121,836, Aug. 6, 1940 (May 13, 1940).

Tumbler. J. E. SPENCE (Hazel-Atlas Glass Co.). U. S. 121,602, July 23, 1940 (May 29, 1940).

Vase. E. W. FUERST (Libbey Glass Co.). U. S. 121,895 and 121,896, Aug. 13, 1940 (Jan. 26, 1940).

Cements

Hardening of magnesia without chloride. V. RODT. *Tonind.-Ztg.*, **62** [91] 1017–18 (1938).—Magnesia can be hardened without the use of the chloride of magnesium and forms a strong, resistant body. In the plastic state the mass can be extruded and hardened by a special process. W.K.

Influence of temperature on strength of Portland cement with and without the addition of silica. K. WÜRTENBERGER. *Tonind.-Ztg.*, **62** [72–73] 787–90; [79] 886–88; [85] 953–56; [86] 962–64; [90] 1005–1007; [96] 1072–74; [97] 1084–86; [99] 1106–1107; [101] 1130–32; [102] 1140–41 (1938).—W. investigated the reaction between cement and fine silica sand at temperatures above boiling in the autoclave. Five types of cement, three commercial products and two special high-lime cements, were used for the test pieces, both by themselves and mixed with sand in varying ratios. One set was stored under standard conditions, another was submerged in water of 20°, 100°, and 180°C., and all were tested for tensile and compressive strength. The strength figures show a minimum at 100°C. and increase with the autoclave treatment due to the formation of new low calcium compounds and a resulting firm interlocking of cement and sand particles. A good cement can carry four parts of sand without much decrease in strength. W.K.

Kinds of minerals in cement. RUDOLF BARTA. *Stavivo*, **20**, 383 (1939); abstracted in *Chem. Zentr.*, **1940, I,** 1405.—$MgSiF_6$ is more advantageous than fluorspar because an addition of 1% (= 0.24% Mg) is sufficient; $MgSiF_6 \cdot 6H_2O$ in amount of 37.94 gm. dissolves easily in 100 cc. of water at 20°. The product is comparatively cheap because it is a by-product in the manufacture of phosphoric acid and superphosphates. M.V.C.

Pottery plaster for molds. CHARLES I. GERBER. *Ceram. Ind.*, **35** [1] 37–38; [2] 39–40 (1940).—Careful control of water-plaster ratio is necessary for uniformity of strength, expansion, absorption, surface texture, and working behavior of molds. G. discusses absorption, effect of mixing on strength, volume changes, setting time, drying, special plasters, and elimination of common troubles such as pinholing, cracking, efflorescence, quick or slow set, and soft molds. Illustrated. L.M.C.

Research on slag cement. Excerpts from report on activity of Research Institute of the Slag Cement Industry in 1937. R. GRÜN. *Tonind.-Ztg.*, **62** [66] 716–18; [67] 729–31; [68] 743–44 (1938).—G. discusses current tests of the various commercial products, special work on cements for road building, comparison of the shrinkage of cement and concrete, and the effect of slag addition upon strength and shrinkage. The results are given in numerous graphs. Plaster cement and cement lime and new methods of casting concrete are dealt with. W.K.

Thermal coefficient of expansion of Portland cement; long-time tests. S. L. MEYERS. *Ind. Eng. Chem.*, **32** [8] 1107–12 (1940).—Illustrated. G.H.

Enamel

Development of enamel furnaces. ZSCHACKE. *Glashütte*, **69** [24] 418–20 (1939).—In 1851 Moritz Vogelgesang published his textbook on the art of enameling on iron. Enameling furnaces and adjoining furnaces of the time, pictured and described in this work, are discussed. M.V.C.

Interpreting the photomicrograph. J. L. MCLAUGHLIN. *Better Enameling*, **11** [4] 12–15 (1940).—The interpretation of photomicrographs as employed in the porcelain enameling industry is discussed together with (1) sample preparation, (2) proper lighting, (3) contrast and details, (4) excessive polishing, (5) scratches, (6) washing, (7) relation of appearance and magnification, and (8) frequency. Illustrated. J.J.H.

Metal bases for enameling. ANON. *Emailwaren-Ind.*, **17** [19–20] 53–55 (1940).—Cast iron or sheet iron and, less often, sheet copper are used as a base for enameling; other metals and the noble metals are used seldom or only for works of art. Sheet iron which has been pickled and heated to redness to make it more workable is freer from flaws and less apt to cause blisters in the enameled ware than sheet metal which has not been so treated. Sheet iron is often designated, according to its method of manufacture, as Siemens-Martin sheet or Thomas sheet iron. Sheet iron contains impurities in small amounts which have a definite effect on the properties of the sheet. A table gives the composition, requirements, and the analyses of some enameled sheet metals. The suitability of a sheet

iron for enameling cannot be learned from the chemical analysis. The question of ductility is important in many cases. A sheet iron having a high extensibility is best for enameling, but it is important that the longitudinal and the transverse expansion be the same. Copper makes sheet iron more malleable, but the maximum addition is 2% (according to Kraze). A basic material (*Spur silisium*) with minimum phosphorus content is also good. The extensibility of sheets can be determined on breaking-test machines, but since these machines are scarce, the testing apparatus of Erichsen, on which sheets 0.1 to 3.0 mm. in thickness are stretched until they break, can be used. In America, and more recently in Germany, sheet iron made of very pure iron (Armco sheet iron) has been used; it is advantageous in that thinner sheets can be used without warping. Metallographic examination of sheet iron discloses a ferrite structure with slag inclusions, etc. If the inclusions are thinly covered with iron, blisters will form when the sheet is enameled because the thin layer of iron is dissolved and the inclusions react with the enamel. Another cause of blisters is the absorption of hydrogen by the sheet metal during pickling. This hydrogen expands when the enameled metal is heated and forms blisters. Inhibitors added to the pickling bath prevent this to some extent. Since enamel adheres mechanically for the most part, a rough surface is important. The thickness of the sheet usually has no effect on enameling. M.V.C.

Refrigerator industry's lowest cost enamel shop. ANON. *Ceram. Ind.*, **35** [1] 31–35 (1940).—An example of production efficiency in a well-organized shop is provided by Servel, Inc., where one employee is needed for each 318 sq. ft. of enamelware finished. There is no trucking in the plant; only 11 workers out of a total of 115 are used for transfer operations. Liners are sprayed, dried, inspected, brushed, and blown-off on the same conveyer. Little storage space is needed in the enamel shop; diagrams are given of the compact shop layout. Ground and cover coat driers are elevated. Enamel is reclaimed and used in amounts up to 30%; the room is always under pressure. The complete schedule of operations is given, along with several shop "kinks" or operating methods, including skimming of the nickel dip sludge and the heating of the ground coat slip in winter. Illustrated. L.M.C.

SEPARATE PUBLICATION

Refining of Enamelers' Clay. G. H. SPENCER-STRONG. *Enamelers' Reference*, No. 3, 11 pp. (1939); *Ceram. Ind.*, **32** [3] 44–46 (1939).—Clays for enameling purposes must (1) have adequate suspension properties, (2) have the ability to absorb the electrolytes which leach out of the frit during the milling operation and for a reasonable time thereafter without any marked change in the set characteristics, (3) give a smooth drain with dipped ware and a satisfactory surface texture with sprayed ware, (4) increase the firing range of the enamel, (5) aid in securing suitable final opacity in the frit without the use of excess quantities of expensive opacifiers, (6) show a good gloss, and (7) not have a tendency to increase scumming. Enameling clays and their formation are discussed. The refining of clay by the dry process used in the past entails loss of the suspension qualities of the clay due to variations in the drier heat or to overheating in drying which are practically unavoidable, metallic contamination from the drying surfaces, and the danger that, either through inefficiency or partial failure of the separating units, contaminating materials in the clay will not be entirely removed therefrom. A new method for the refining of enamelers' clay does away with the requirements for predrying of the clay, grinds the clay to a greater degree of fineness than is possible with ordinary methods, and entirely removes the contaminating products without the use of screens and magnetic separators in a single operation. It consists of an air reduction mill known as a "Micronizer" (see "Jet...," *Ceram. Abs.*, **17** [10] 334 (1938)). The clay produced by this method has an average grain size of four microns or less, is essentially free from contamination, either organic or inorganic, and has a moisture content of only about 2%. Illustrated.

PATENTS

Acid-resisting enamel. LUDWIG STUCKERT (Deutsche Gold- und Silber-Scheideanstalt). U. S. 2,209,585, July 30, 1940 (Aug. 18, 1938).—An acid-resistant enamel especially suitable for application to sheet-metal surfaces comprises silica, an alkali-metal oxide selected from the group which consists of the oxides of sodium and potassium, zinc oxide, calcium oxide, and lithium oxide, the lithium oxide being present in amounts ranging from 1 to 3%, based on the total weight of the enamel, and in no case exceeding 15% by weight of the total alkali content present in the composition, the enamel being substantially completely free from fluorine.

Ceramic-coated article. W. J. SCOTT (Western Electric Co., Inc.). U. S. 2,211,170, Aug. 13, 1940 (Sept. 18, 1937).—A method of producing a contrastingly colored enamel coating on a base with an absence of reboiling comprises the steps of applying a finely divided vitreous enamel of specified color on the base and excluding particles that have been eliminated when the enamel is mixed with a relatively larger volume of water and the supernatant liquid is decanted after settling, fusing the enamel on the base, applying a second enamel of contrasting color to portions of the fused enamel, and refiring the base to fuse the second enamel.

Enamelware making. J. E. ROSENBERG (Enamelers Guild, Inc.). U. S. 2,210,556, Aug. 6, 1940 (July 13, 1939).—A method of producing an article of enamelware of crinkle finish consists in spreading upon the surface of the article to be enameled a vitreous coating that includes a pigment of reducing nature, overspraying such coating with a coating of milled clear enamel that carries, in association with a fluoride, an antimony compound of trivalent character, firing in an oxidizing atmosphere, and cooling.

Glass

Batch segregation. ANON. *Ceram. Ind.*, **35** [2] 31–34 (1940).—The segregation of particles of a batch mixture is influenced by (1) particle size, (2) particle shape, (3) density, and (4) surface characteristics. Finer particles reduce segregation, within the commercial size range. The recommended grading for glass sand is given, together with analyses of particles of satisfactory soda ash and lime. Mixing time must be closely controlled. Segregation occurs during the transportation of the mixed batch on flat conveyers. It is advantageous to drop the finished batch into the container as a unit rather than in a continuous stream. Improved batch handling methods which reduce segregation are described. Comments on this article by five selected men in the glass industry are included. Illustrated. L.M.C.

Blast-furnace slag as raw material for glass. ZDENĚK SCHAEFER. *Sklářské Rozhledy*, **16** [9–10] 171–75 (1939); abstracted in *Chem. Zentr.*, **1940, I,** 1404.—S. reviews the experiments of Russian, German, and American research men. Blast-furnace slags are analyzed, and the possibility of replacing costly metal oxides with blast-furnace slag in the manufacture of colored glass is discussed. M.V.C.

Bottle-machine molds wear out faster in high-speed production. F. G. PASOTTI. *Ceram. Ind.*, **35** [1] 36 (1940).—P. describes research being conducted at the University of Illinois on Owens suction blanks for bottle machines. This research was undertaken because these blanks check or crack more readily and to a greater degree than any other type of mold. Blanks made at the same time from the same heat in the foundry behave differently in production. Ten or fifteen years ago it was common to obtain as many as 100,000 gross bottles per set of molds, on account of the slow speeds and greater weight

of glass per container. Now molds fail, on an average, at 45,000 gross bottles. While blank molds usually give the least service from the point of view of checking, some blow molds check when the volume-surface ratio is out of balance. This may be caused by bad design or by attempting to run a larger job on the glass machine than was intended by the designer. The average life of a set of molds for the various bottle machines is given. L.M.C.

Carbon-yellow glasses. O. PŘIDAL. *Sklářské Rozhledy*, **16** [9–10] 158–64 (1939); abstracted in *Chem. Zentr.*, **1940, I,** 1404–1405.—Experiments were made in an electric melting furnace in neutral atmosphere to determine how intense a coloring can be obtained with coal (or other substances containing C) and sulfate and in what measure the intensity depends on the quantity of coal and sulfate used. The glass was cast in molds and ground to plates 5 mm. thick. Its absorption was tested with the naked eye and with different wave lengths in the "Domsi" monochromator (tables and diagrams). Glasses with high alkali content are more sensitive to polysulfide and are redder in color than glasses with low alkali content (wine yellow). The addition of sulfate or materials containing S is always necessary if there is not enough S already in the batch. Graphite is the best of the products containing C because it can be measured accurately; cheaper graphite containing S can replace sulfate partially or entirely. For ordinary glass batches containing no S, the best proportion for 100 kgm. sand is 0.7 to 1 kgm. sulfate and 2 kgm. C. Oxidizing substances are injurious. The addition of fluorspar helps prevent the formation of blisters. M.V.C.

Chemical action of dilute sulfuric acid on lead glasses. A. VAŠÍČEK. *Glastech. Ber.*, **18** [2] 45–49 (1940).—Thin films were produced on glasses by treatment with H_2SO_4. The films were examined with the use of a polarization spectrometer. V. established the fact that the ellipticity of the reflected light was a sensitive measure of changes in the films. Index of refraction and thickness can also be determined. The index of the films thus formed corresponds to that of amorphous silica. See "Artificially . . .," *Ceram. Abs.*, **19** [1] 8 (1940). J.F.H.

Chromium plating of molds for glassware. S. C. BALDERSON. *Glass*, **17** [6] 193 (1940).—Although extensive tests have proved that glass molds can be plated satisfactorily with chromium, the method has not been accepted generally, due largely to inexperience in preparing the molds and performing the plating. Chromium-plated molds will withstand for a short time temperatures up to 2700°F.; above 1800°F. the chromium gradually diffuses into the iron. A useful life of 500 hr. may be expected at a working temperature of 1930°F., while at 2370°F., the chromium plating will last only 2 to 3 days. The cost of plating, while usually high, is determined by the intricacy of the mold, which requires a complicated system of anodes conforming closely to the contour of the mold. Due to differences in thermal expansion, the chromium plating has a tendency to crack and flake off. B.C.R.

Color of soda-lime-silica glasses containing iron oxide and manganese oxide. A. LAWTON, A. J. HOLLAND, AND W. E. S. TURNER. *Jour. Soc. Glass Tech.*, **24** [102] 73–92T (1940).—Twenty-six soda-lime-silica glasses containing iron oxide and manganese oxide singly and in combination were prepared by melting them in platinum in an electric furnace with slightly oxidizing conditions and grinding the cast disks to a known thickness, the standard of reference being 2 mm. The light transmission in the visible spectrum was then measured spectrophotometrically. In the glass containing iron oxide only, that oxide was added as Fe_2O_3 in amounts ranging from 2.92 to 9.3%; the proportions of FeO and Fe_2O_3 in the glass showed a slight falling off, viz., from 9.93 to 7.80% of the total iron as FeO, with rise in total concentration; the successive transmission curves showed a relative increase in transmission at the long wave-length end and a falling off in over-all transmission from 61.6 to 6.2% for the change in concentration stated. The manganese oxide was added as MnO_2, and analyses were not made to ascertain the respective proportions of MnO_2 and other oxides resulting from the liberation of oxygen. For glasses in the preparation of which MnO_2 had been added in amounts equivalent to 3.1 to 9.62%, the curves all possessed the same form, showing strong absorption in the green and blue-green; the over-all transmission ranged from 5.14 to 0.02%. Several series of glasses were prepared in which Fe_2O_3 and MnO_2 were used jointly in total amounts ranging from 3.1 to 17.54% but in varying ratios. Marked increase in transmission took place when iron oxide was added to a glass containing manganese oxide. A glass containing 3% of MnO_2 thus had an over-all transmission of 6% but an addition of 3% of Fe_2O_3 increased it to 65%. Iron oxide-manganese oxide glasses in which the iron oxide content was equal to the manganese oxide content did not become opaque until a concentration of 10% of iron oxide plus 10% of manganese oxide was reached. For a given concentration of combined iron oxide and manganese oxide, the glass with the highest over-all transmission was the one which contained iron and manganese oxides in the ratio of approximately 2:3. Glasses in which the ratio of Fe_2O_3 to MnO_2 was 1:2 and 1:1 also had high over-all transmissions. In applying the results to commercial practice, the importance of the conditions of oxide concentration, time of melting, temperature, batch composition, and furnace atmosphere was emphasized. In the manufacture of commercial amber-colored soda-lime-silica glasses, using Fe_2O_3 and MnO_2 as coloring agents, the equilibrium conditions as defined and aimed at in preparing the specimens for the investigation described are rarely attained. The resulting colors in commercial practice are unlikely to be repeated in different factories or in any one factory when the same batch is used for glass melted in gas-fired furnaces, in one case in a pot and in the other in a tank. G.R.S.

Course of dispersion of the Jena optical glasses between 400 and 800 mμ and its representation by Hartmann's interpolation formula. H. SLEVOGT. *Z. Instrumentenk.*, **60** [2] 37–48 (1940).—Complete tables for the determination of the optical constants of all Jena (Schott) optical glasses are given. Their application to the selection of lens systems and the calculation of refractive indices and correction values are explained in full. The refractive index of glasses is determined from $n(\lambda) = n_0 + [C/(\lambda - \lambda_0)]\alpha$; the constant C can be taken from the tables; this is more accurate than the graphic interpolation of the indices before C could be calculated exactly as was usually done. Fifteen references. M.H.

Development of a prestressed glass insulator. P. M. HOGG. *Engineering*, **149** [3876] 449 (1940); *Glass*, **17** [5] 142 (1940).—The prestressing of cast glass insulators is accomplished by heating the glass considerably above its strain temperature and then cooling it rapidly with an air blast under controlled conditions so that the outer surface is under compression. All insulators are subjected to a routine thermal shock test in which the pieces are introduced into a kiln at 550°C. and allowed to remain there until the transient temperature gradient in the glass has reached a maximum. Prestressed insulators possess an appreciably greater resistance to both mechanical and electrical shock. B.C.R.

Display glass. ANON. *Glass*, **17** [3] 83 (1940).—To overcome the color interference of plate glass due to its green tinge, a new display glass called "Spectralite" has been developed and is produced in two shades: "Spectralite A," which is very slightly pink with the green tinge completely removed, is used for displays of light-colored materials; "Spectralite B," which has a more decided pink color, is used for objects having a pink, red, brown, or yellow color. B.C.R.

Effect of alumina on devitrification of sodium oxide-dolomite lime-silica glasses. W. B. SILVERMAN. *Jour. Amer. Ceram. Soc.*, **23** [9] 274–81 (1940).

Effect of alumina on the expansion and deformation temperature of soda-lime-silica glasses. WILLIAM B. SILVERMAN. *Jour. Soc. Glass Tech.*, **24** [102] 59–72T (1940).—S. presents the coefficients of expansion between 80° and 170°C. and the deformation points of a systematic series of soda-lime-silica glasses as measured by the inter-

ferometer method. The range of composition covered extends from 11 to 19 Na_2O, 6 to 16 CaO, 0 to 8 Al_2O_3, and 59 to 79% SiO_2. G.R.S.

Electrochemical measurement of the partial pressure of oxygen: I, Investigation of oxidation equilibria. PAUL CSAKI AND ADOLF DIETZEL. *Glastech. Ber.*, **18** [2] 33–45 (1940).—A concentration cell such as the following was used: Pt in O_2 ($p = 1$)/glass melt 1—glass melt x/Pt in O_2 ($p = x$). The platinum electrodes were enclosed in platinum tubes which contacted the molten glass surface. The platinum tubes in turn were cemented to porcelain tubes above, through which another porcelain tube passed to introduce the electrode gases and which served to support the electrodes. The two glass melts were contained in platinum crucibles not in contact, the electrical circuit being completed by a bridge. The bridge was a borosilicate glass rod coated with the base glass which was borax. The crucibles were surrounded by a suitable furnace. Porcelain tubes were first used to enclose the electrodes, but irregularities resulted in the potential due to the dissolving of the refractory. Later experiments with refractories introduced as small pellets showed that characteristic potentials can be obtained, and the method may thus prove extremely useful in studying corrosion, e.g., using oxygen and air as rinse gases at 830°C., a constant and reproducible potential of 0.0325 volt is rapidly attained, which is about 10% lower than the calculated value. A study of melts made under CO_2 shows how the potential depends on gas diffusion through the melt. Using air as electrode gas, such a melt required approximately 100 min. to reach equilibrium potential. A series of melts with 1% total iron as Fe_2O_3 was made under various oxidation-reduction conditions using pure H_2, N_2-H_2 mixtures, CO_2, and air. Samples were analyzed chemically and photometrically to establish the FeO and Fe_2O_3 contents. Plotting e.m.f. measurements against Fe(%) gives the typical potential curve for the equilibrium. J.F.H.

Equipment halves inspection cost. L. G. JACQUES. *Factory Management & Maintenance*, **98** [6] 68, 130 (1940). —J. explains how the designing of a continuous conveyer inspection rack enables 16,000 pieces of flat glass to be inspected per day by three inspectors. Before the rack was used the same amount of glass inspection required 20 inspectors. Counting the truckers and handlers, nine men now do the work formerly performed by 23 men. The old plan required 1200 sq. ft. of floor space. The new one uses 400 sq. ft. J.L.G.

Glass fiber as a wire covering. ANON. *Electrician*, **125**, 19 (1940).—Glass fiber is a class B material capable of operating at temperatures which would quickly destroy cotton, silk, enamel, and similar organic materials. The dielectric strength of Lewcoglass is superior to that of asbestos. Individual fibers of glass will not absorb moisture, but surface absorption may take place. When transferred from a moist to a dry atmosphere, glass fiber loses absorbed moisture much more quickly than cotton or asbestos, a steady state being reached in about 5 min. Cotton and asbestos require hours to reach this steady state. Good heat conductivity helps cool running and increases the output from machines of a given size. In this respect glass fiber is comparable to silk, cotton, paper, etc., and is better than asbestos. Standard impregnation methods may be employed, and, since the covering is chemically inert, the possibility of interaction with impregnants and solvents is remote. The abrasion resistance of glass may be inferior to that of textile coverings on sharp-edged surfaces but is superior for smooth rubbing surfaces. It is, however, adequate for coil applications, and there is no likelihood of the loosening or stripping of the covering provided that proper tensioning devices are used. The high space factor of glass permits an increase of 10 to 15% in copper in a machine over that in a machine with asbestos insulation. Increased rating results from putting more current into apparatus without any corresponding increase in losses. The shorter heat path due to the thin covering is also a factor. A further gain is possible by increase of the operating temperature. The use of glass is said to have doubled the amperage of otherwise identical welding generators. H.K.R.

Heat utilization. C. H. MODES. *Ceram. Ind.*, **35** [1] 44–47 (1940).—M. discusses the effect on the temperature of combustion in a glass tank if natural gas is burned with (1) the theoretical amount of cold dry air, (2) requisite air preheated to 500°C. and preheated to 1000°C., (3) 25% more air than theoretically necessary (air cold, preheated to 500°C. and preheated to 1000°C.), and (4) a smaller quantity of air than theoretically necessary so that 5% of gas will remain unburned (air cold, preheated to 500°C. and preheated to 1000°C.). Results indicate that the highest efficiency will be obtained through a nearly balanced combustion where excess oxygen is between 2 and 5%. Illustrated. L.M.C.

History of mirrors: I–IV. BRUNO SCHWEIG. *Glass*, **17** [2] 50; [3] 81; [4] 108; [6] 180 (1940).—S. gives a historical account of the development in the manufacture and uses of mirrors. B.C.R.

Influence of shape of cross section and surface condition on breaking strength of glass rods. G. SCHUMANN. *Z. Physik*, **98** [9–10] 605–609 (1936); *Science Abs.-A*, **39** [459] 229 (1936).—S. shows that (1) the average deviation of the values of the breaking stress of glass rods is influenced by the form of the cross section, (2) the mechanical surface state leaves the material curve unchanged, and (3) a lowering of the surface energy by adsorbed liquids produces greater reflecting surface and lower breaking strength. H.K.R.

"Kraut stems" to cocktail glasses. History of drinking glasses. TECHNICAL GROUP OF THE HOLLOW GLASS INDUSTRY. *Glashütte*, **69** [25] 435–36 (1939).—With the growth of glass production, drinking cups of clay, wood, and precious metal for wine and beer were replaced more and more by glass cups, until finally the name of the material, glass, came to be adopted for the container itself. A hemisphere or cup was the original form; gradually, embellishments such as glass bands or facets were added. Bowl forms, with glass drops fused on, came into use; the glass resembled a defoliated cabbage stem with its bulging body and knotty surface, and was the highest development of this form. The "Spechter" glass was of a high narrow cylindrical form with a lip edge. The "Roman" glass has been preserved to the present time though not in precisely the same form. It was first a cylindrical bowl with the upper smooth part separated from the lower knotty part by a glass band; it was then divided into cup, stem, and foot. It came originally from Cologne; a Roman colony founded there might have introduced the art of glassmaking from Rome. The form and decoration of glasses gradually improved; cutting, engraving, etching, flashing, and painting with enamel elevated glassware to the rank of works of art. Today the form of glasses is fixed, for the most part, for wines and some other alcoholic beverages. M.V.C.

Raw and auxiliary materials for the production of glass in the Sudetenland. RUDOLF SCHMIDT. *Glashütte*, **69** [20] 353–57 (1939).—With the annexation of the Sudetenland, Germany acquired 63% of the important Czechoslovakian glass plants and obtained access to rich deposits of sand, feldspar, phonolite, lime and dolomite, graphite, and the auxiliary materials, earths, pot clays, kaolin, and coal, which are described. M.V.C.

Relation of electrical conductivity to chemical composition of glass. A. E. BADGER AND J. F. WHITE. *Jour. Amer. Ceram. Soc.*, **23** [9] 271–74 (1940).

Requirements for the most important raw materials for the glass batch and their physical state. ANON. *Glashütte*, **69** [21] 369–72; [22] 388–91; [23] 403–405 (1939).—Raw materials for the glass batch vary in their natural state and composition and require careful supervision. The principal raw materials are characterized and their suitability with regard to grain size and other properties is discussed as follows: (1) Sand for the glass melt can be obtained in the proper form for all requirements, but it is not known whether its natural grain size is especially favorable technically for melting or whether it could be improved upon. (2) Soda exists in different forms, of

which the "heavy" and granular form is regarded as the best. (3) Sulfate in the commercial form for glassmelting fills all requirements. (4) Coke powder finely divided has proved to be the best form of reducer. It is possible that with a better method of dispersion of the coal in sulfate, a larger amount of it instead of soda might be of advantage technically and economically for many kinds of glass. (5) Lime and dolomite vary when ground because of their variable mineral state, but they can be used safely in the batch in this form provided that not too large amounts are added. M.V.C.

Scratching of glass by metals. L. G. GHERING AND J. C. TURNBULL. *Bull. Amer. Ceram. Soc.*, **19** [8] 290–94 (1940).

State Technical School for the Glass Industry in Haida in the Sudetenland and its development. ERICH BÖHMER. *Glashütte*, **69** [25] 433–35 (1939).—The glass refining industry in the Sudetenland began in 1530 when the first glass plant was built at Falkenau in Haida. At first green glass called "forest glass" was made. This was gradually improved until a crystal clear glass of great beauty was produced. In 1870, through the joint action of the State and industry, a school for the designing and fashioning of glass and for wood carving was founded; it soon became an outstanding artcraft school. At the present time students receive artistic, theoretical, and handicraft training. During the three- to four-year course, drawing from nature, designing, technique, and practical training in workshops are studied. See "Bohemian...," *Ceram. Abs.*, **18** [8] 205 (1939). M.V.C.

SEPARATE PUBLICATION

Short Story of Technical Glassware. CORNING GLASS WORKS, Corning, N. Y., 1938. 30 pp., 21 illustrations.—A historical sketch is given, and present methods of production are described. G.H.

PATENTS

Apparatus for bending vitreous tubing. C. A. BROWN AND F. B. VAN SICKLE (General Electric Co.). U. S. 2,208,958, July 23, 1940 (Nov. 18, 1937).

Apparatus for glazing glassware. C. T. STEWART AND C. O. STEWART (Glapat Corp.). U. S. 2,209,252, July 23, 1940 (Feb. 11, 1937).

Apparatus for producing polished glass strip. PILKINGTON BROS., LTD., AND F. B. WALDRON. Brit. 523,427, July 24, 1940 (Jan. 6, 1939).

Apparatus for surfacing plate glass. R. D. BOLE AND E. A. FUSCA (Pittsburgh Plate Glass Co.). U. S. 2,209,505, July 30, 1940 (March 29, 1938).

Building block. KARL SNIPISCHKI (Samuel Gartner). U. S. 2,211,177, Aug. 13, 1940 (May 10, 1938).

Ceramic materials adapted to be sealed to glass. GENERAL ELECTRIC CO., LTD., AND J. R. LAIT. Brit. 522,586, July 3, 1940 (Dec. 9, 1938).

Compound glass. HOWARD W. MATHESON (Shawinigan Chemicals, Ltd.). Can. 388,743, May 14, 1940 (May 29, 1935). G.M.H.

Contact lens and method of making. E. D. TILLYER (American Optical Co.). U. S. 2,211,086, Aug. 13, 1940 (Dec. 8, 1937).

Crucible glass feeder. C. C. COOK AND D. W. COOK. U. S. 2,210,617, Aug. 6, 1940 (Aug. 5, 1938).

Device for cutting or scoring necks of bottles. A. J. MCGANN. U. S. 2,209,701, July 30, 1940 (March 8, 1938).

Electrode for glassmelting furnace. R. G. EHMAN AND H. F. HITNER (Pittsburgh Plate Glass Co.). U. S. 2,209,515, July 30, 1940 (Jan. 11, 1939).

Foliated glass manufacturing apparatus. EDMUND H. WELLECH AND WALTER C. WEBER (Corning Glass Works). Can. 388,814, May 21, 1940 (April 11, 1938; in U. S. May 25, 1937). G.M.H.

Glass building block. HARRY S. HOWER (Corning Glass Works). Can. 388,813, May 21, 1940 (Feb. 8, 1938; in U. S. Feb. 11, 1937). G.M.H.

Glass charge delivery apparatus and method. K. E. PEILER (Hartford-Empire Co.). U. S. 2,209,018, July 23, 1940 (July 30, 1937).

Glass fiber mat making apparatus. ALFRED L. FORSTER (Fiberglas Canada, Ltd.). Can. 389,312, June 11, 1940 (Feb. 28, 1938). G.M.H.

Glass-tempering method. C. J. PHILLIPS (Corning Glass Works). Can. 388,811, May 21, 1940 (Nov. 30, 1937; in U. S. Dec. 28, 1936). G.M.H.

Glass thread. ALDO CERETTI (Fiberglas Canada, Ltd.). Can. 389,610, June 25, 1940 (Dec. 24, 1937). G.M.H.

Glass thread drawing system. ALDO CERETTI AND PIERO MODIGLIANI (Fiberglas Canada, Ltd.). Can. 389,611, June 25, 1940 (March 29, 1938). G.M.H.

Glassware mold. T. D. SAUNDERS (Dunbar Glass Corp.). U. S. 2,209,936 and 2,209,937, July 30, 1940 (March 29, 1938).

Glassware mold assembly. T. F. PEARSON (Crown Cork & Seal Co., Inc.). Can. 388,663, May 14, 1940 (Sept. 15, 1936). G.M.H.

Glass wool making apparatus. L. D. SOUBIER (Fiberglas Canada, Ltd.). Can. 389,311, June 11, 1940 (Feb. 23, 1938). J. H. THOMAS (Fiberglas Canada, Ltd.). Can. 389,313, June 11, 1940 (May 5, 1938; in U. S. May 11, 1937). G.M.H.

Glassworking apparatus. RAY A. HINKLEY AND EDMUND H. WELLECH (Corning Glass Works). Can. 388,815, May 21, 1940 (Dec. 20, 1938; in U. S. Feb. 28, 1938). G.M.H.

Laminated safety glass. G. B. WATKINS AND J. D. RYAN (Libbey-Owens-Ford Glass Co.). U. S. 2,209,435, July 30, 1940 (Nov. 15, 1935).

Lead glass. H. H. BLAU (Corning Glass Works). Can. 388,812, May 21, 1940 (Nov. 30, 1937; in U. S. Dec. 29, 1936). G.M.H.

Lens-edging machine. A. E. MAYNARD (American Optical Co.). U. S. 2,209,605, July 30, 1940 (April 25, 1938).

Manufacture of ruby glass. E. I. DU PONT DE NEMOURS & Co. Brit. 522,634, July 3, 1940 (Dec. 15, 1937).

Manufacture of vitreous envelopes, more particularly of cathode-ray tubes, through which pass leading-in wires. GENERAL ELECTRIC CO., LTD., J. RICHARDS, AND G. W. WARREN. Brit. 522,444, July 3, 1940 (Dec. 8, 1938).

Mineral composition for use in glass manufacture. C. H. PEDDRICK, JR. (Feldspathic Research Corp.). U. S. 2,210,254, Aug. 6, 1940 (June 9, 1936).—A glass batch ingredient comprises a mixture of pyrophyllite and feldspar.

Optical-lens manufacture. RAOUL FRITZ. Can. 388,897, May 28, 1940 (Oct. 16, 1937). G.M.H.

Siliceous product and method of making. GEORGE KALOUSTIAN (Cobrecite Corp.). U. S. 2,209,163, July 23, 1940 (July 8, 1939).—The method of making an inorganic water-insoluble material in the form of a unitary block having a multiplicity of intercommunicating pores or voids therein comprises admixing particles of siliceous material with an alkaline reacting fluxing material and with a removable inert material of higher melting point than the fluxing agent, subjecting the resulting mixture to the action of heat sufficient to cause the formation of a water-insoluble bond between the particles of siliceous material at their points of contact by interaction between the particles and the agent, cooling the bonded mass, and removing the inert material.

Siliceous products and methods of making. H. S. NEVIN AND GEORGE KALOUSTIAN (Cobrecite Corp.). U. S. 2,209,170, July 23, 1940 (July 8, 1939).—The method of making a unitary vitrified block having a multiplicity of intercommunicating pores or voids therein comprises mixing from 5 to 9 parts of crushed volcanic glass with approximately 1 part of water and approximately 1 part of an alkaline reacting fluxing agent and firing the resulting mixture at a temperature sufficient to cause the formation of a water-insoluble bond between the particles primarily at their points of contact by interaction between the particles and the agent.

Sodium calcium borosilicate glass. U. E. BOWES (Fiberglas Canada, Ltd.). Can. 388,836, May 21, 1940 (Dec. 2, 1937; in U. S. Dec. 30, 1936). G.M.H.

Textile material. GAMES SLAYTER (Fiberglas Canada, Ltd.). Can. 389,609, June 25, 1940 (March 5, 1937). G.M.H.

Structural Clay Products

Brick acceptance test investigation. H. Z. SCHOFIELD. *Dependable Highways*, No. 167, pp. 8–10 (1940).—S. outlines the U. S. Bureau of Public Roads, the State of Ohio Department of Highways, and the National Paving Brick Association cooperative investigation of paving brick acceptance tests, the first phase of which began in 1938. The object of the investigation is to develop a test procedure capable of appraising the fitness of a given lot of paving brick. P.S.D.

Construction of a brick storm drain in Ashtabula, Ohio F. A. COLLINS. *Dependable Highways*, No. 167, pp. 11–14 (1940).—C. discusses construction details and gives cost data for a 9851-ft. storm drain designed to serve an area of 970 acres. P.S.D.

Fired earth in the building. H. HECHT. *Tonind.-Ztg.*, **62** [74–75] 809–20 (1938).—H. gives a history of the use of brick for building and discusses modern tendencies and improvements in the production and use of brick for all kinds of construction. Numerous illustrations of old and new buildings form an essential part of the paper. W.K.

Hollow ware from sandy clay. ANON. *Tonind.-Ztg.*, **63** [49] 563–64; [51] 585–86 (1939).—The production of hollow ware from sandy clay requires the addition of some fat clay. To keep the percentage of this clay low, the coarse sand can be removed from part of the local clay by special machinery. The fat clay should be added as fine powder. Deairing greatly improves the plasticity of the body. A good auger machine and a properly adjusted die are important. W.K.

Moisture content of air-dried brick. T. F. MERTEN. *Tonind-Ztg.*, **62** [86] 961–62 (1938).—The drying behavior of brick made from various layers of the clay bank was studied, and the figures are given. Air-dried brick contained as an average 1.41% moisture. W.K.

Properties of brick in the light of recent construction. H. HECHT. *Tonind.-Ztg.*, **62** [99] 1103–1107; [100] 1116–1120; [101] 1127–1129 (1938).—Standard brick from various sources, vitrified brick, hollow brick, porous brick, and roof tile were tested for properties such as weight by volume, transverse and compressive strength, true and apparent porosity, pore size, rate of absorption, permeability to water and air, resistance to acid, and heat conductivity. The figures are given in tables and are correlated in graphs. Their relationship or lack of relationship is studied and discussed. W.K.

Usual temperatures for unloading brick kilns. OPPERMANN. *Tonind.-Ztg.*, **63** [47] 539–41 (1939).—Measurements of the temperature in the ring kiln at the time of unloading were made in several plants by government officials and by the plant management. The results are tabulated together with the atmospheric temperature and other data. The highest temperature registered was 70°C., but on the whole 50°C. was seldom exceeded. The temperature of the ash on the floor, however, was, in one instance, as high as 200°C. W.K.

Vibrated monolithic brick tests. ANON. *Dependable Highways*, No. 167, p. 10 (1940).—A brief outline is given of a cooperative program of tests to determine the strength of vibrated monolithic brick pavement slabs. P.S.D.

PATENTS

Building block or brick. J. J. CANTWELL (Speedbrick Corp.). Can. 389,783, July 2, 1940 (May 6, 1939). G.M.H.

Manufacture of wire-cut brick, tile, etc. F. P. JONES AND F. M. JONES. Brit. 522,638, July 3, 1940 (Dec. 16, 1938).

Method and means of forming brick and tile. B. J. CHAMBLIN. U. S. 2,209,643, July 30, 1940 (Aug. 19, 1936).

Refractories

Adhering strength of sprayed refractories. R. RASCH. *Tonind.-Ztg.*, **64** [2] 13 (1940).—R. discusses the causes for the falling away of sprayed refractory coatings in furnaces. Although the heat resistance of the coating substance is usually tested, its adhering properties are often neglected. The most frequent cause for the falling away of refractory coatings is the formation of a steam cushion produced by the mixing water when it is sprayed on the hot furnace masonry; this prevents unification through sintering. R. describes a laboratory method of testing the adhering strength of sprayed-on refractories by subjecting them to conditions equal to or even more severe than those prevailing in the furnace. A test dealing with a coating for a silica coke-oven chamber is described. F.E.S.

Basic open-hearth furnace. A. H. MELDRUM. *Eng. Jour.*, **23** [6] 265 (1940).—M. describes the construction and operation of a basic open-hearth furnace. B.C.R.

Clay products for technical use. W. STEGER. *Tonind.-Ztg.*, **62** [74–75] 821–27 (1938).—The improvement of ceramic products for technical purposes is discussed. For the production of iron and steel, better refractory materials such as magnesia and chromite brick have been developed. The resistance of tank blocks has been increased by increasing the alumina and by the casting process. Special brick have been developed for cement kilns. Insulating refractory material has been produced. Acid-resistant brick and stoneware are today essential equipment for the chemical industry. Complete machinery is made of acid-resisting stoneware. W.K.

Crazing of pots for fusing glass during tempering. E. S. *Sprechsaal*, **73** [20] 176 (1940).—Pots, whether made of well prepared acid or base masses or of masses of inferior quality, can be tempered without the formation of cracks if properly treated. A long tempering time gave worse results than a shorter tempering time in cases studied in practice. Pots should be completely dried before tempering; the tempering furnace must be so operated as to assure a constant and even heat. The charge should not be exposed to direct heat. M.V.C.

Expanding use of superduty fire-clay brick. C. E. BALES. *Ohio State Univ. Eng. Expt. Station News*, **12** [3] 15–16 (1940.)—These brick are made of carefully selected clays and are quite different from regular fire-clay brick. They resist spalling and certain slags, carry high loads, and are practically stable in volume at high temperature. They are used in power plant furnaces; in parts of enameling furnaces, frit furnaces, glass tanks, pottery kilns, and sodium silicate furnaces; in the walls and bottoms of malleable iron furnaces; in forge and welding furnaces; in the regenerator walls and arches of open hearths; in blast-furnace stoves; in lead, zinc, brass, and zinc oxide furnaces; and in lime kilns. They are better than silica brick for intermittent use in electric furnaces melting steel or alloy irons. W.D.F.

Laboratory course in refractories. NELSON W. TAYLOR. *Bull. Amer. Ceram. Soc.*, **19** [8] 315–17 (1940).

Lightweight refractory brick. I. L. MOVSHEVICH. *Vestnik Inzhenerov & Tekh.*, **1938**, No. 12, p. 763; abstracted in *Chem. Zentr.*, **1939, I**, 5026.—A new method

of producing lightweight refractory brick comprises the addition of small amounts of foam formers (colophony, soap, saponin) to a mix of 80% grog (grain size 0.5 mm.) and 20% clay. The addition of 2 to 3% coal, wood, etc., is recommended. Drying takes about 45 hr. at 70°; firing is done at 1320°. The finished product has a weight of 0.58 to 0.85, a resistance to pressure of 20 to 114 kgm. per sq. cm., a thermal conductivity of 0.4 to 0.5 cal./m./degree/hr., and refractoriness up to 1690° or 1750°.

M.V.C.

Refractories and the modern steelworks. C. P. Warden. *Refrac. Jour.*, **15** [8] 347 (1939).—W. reviews the uses and desired properties of refractories for the various installations in the steel industry. B.C.R.

Refractories in the sugar industry. Suydam. *Internat. Sugar Jour.*, p. 182 (1939); abstracted in *Refrac. Jour.*, **15** [8] 392 (1939).—Potassium salts may exist in the bagasse furnace atmosphere in sufficient quantities to affect the refractory lining to a greater extent than is generally realized and to lower the P.C.E. value, especially that of brick containing uncombined silica. Ash, as long as it does not remelt or accumulate to such an extent as to retard the gas flow or to reduce effective furnace volumes, serves as a protection for the brickwork against the effects of sudden temperature changes. Conditions to which refractories are exposed in bagasse-fired furnaces are far more severe than might be anticipated from the temperature alone, and low maintenance costs and economical operation can be secured only by correct furnace design and by the selection of the type of refractories best suited to the conditions. B.C.R.

Refractories used in high-frequency electric melting of steel and alloys. B. W. Magalis. *Bull. Amer. Ceram. Soc.*, **19** [8] 298–301 (1940).

Refractory properties of topaz. R. S. Bradley, F. W. Schroeder, and W. D. Keller. *Jour. Amer. Ceram. Soc.*, **23** [9] 265–70 (1940).

Trends in refractories for the basic open-hearth furnace: I. R. P. Heuer. *Metals & Alloys*, **11** [4] 95–98 (1940).—H. discusses the substitution of basic brick for silica brick in the roof and other parts of an open-hearth furnace. He points out that the shortcomings of silica brick can be traced chiefly to the low melting point of silica (1710°C. (3110°F.)) and the ease with which it can be fluxed by basic oxides. The progress made in basic brick during the past 10 years is discussed. A new method includes "gap-sizing" of the particles and then forming brick under pressures of 10,000 lb. per sq. in. The increased strength obtained by this method makes it possible to produce brick without the conventional firing in kilns. A typical installation is described in detail, and the results of a petrographic examination on chrome-magnesite brick after a campaign in the furnace are discussed. Fusion tests on the altered section of brick remaining at the hot working face showed a P.C.E. value in excess of cone 38 (1835°C. (3335°F.)). **II.** *Ibid.*, [5] 152–55.—The construction of suspended basic open-hearth roofs is discussed. In describing the iron oxide attack, H. points out that the iron oxides flux magnesite slightly at high temperatures and cause shrinkage of the brick instead of expansion. Some chrome-magnesite brick are not sensitive to iron oxide attack. A detailed description is given of other parts of the open-hearth furnace, and the economy of a basic open-hearth roof is discussed. References are given. Illustrated. J.J.H.

Use of aluminum metal in the ceramic industry: I, Properties of refractories produced with mixtures of aluminum, fire clay, and grog. H. G. Schurecht and H. I. Sephton. *Jour. Amer. Ceram. Soc.*, **23** [9] 259–64 (1940).

PATENTS

Bonding of calcium silicates. N. P. Pitt and E. G. Baker (Canadian Refractories, Ltd.). U. S. 2,210,326, Aug. 6, 1940 (April 1, 1937).—A method of bonding, without firing, materials containing nonhydrating calcium silicate having a lime to silica ratio between 1.4 and 5.0 comprises mixing such material with water and a water-soluble bonding agent being one of a group of compounds consisting of the alkali-metal carbonates, fluorides, sulfides, arsenates, and hydroxides, whose negative radicals when combined exclusively with hydrogen are, in water, weak electrolytes, shaping the mass into any desired form, and drying.

Furnace bottom. Fritz Keydel (Didier Werke A.-G.). U. S. 2,211,127, Aug. 13, 1940 (Aug. 5, 1938).—A furnace bottom has an annular wall and a bottom, the bottom comprising a layer of parallel strings of blocks with ends which incline upwardly toward the vertical plane through the middle of the strings whereby the inner end of each block overlaps the outer end of the block next inwardly thereof, the wall having faces that slope upwardly and inwardly above and conformably with the outer ends of the endmost blocks of the respective strings.

Insulating firebrick manufacture. C. L. Norton, Jr. (Babcock & Wilcox Co.). Can. 389,985, July 16, 1940 (Feb. 25, 1938; in U. S. Feb. 27, 1937). G.M.H.

Manufacture of highly reactive alumina. Erich Wiedbrauck and Hans Ginsberg (Th. Goldschmidt A.-G. and Vereinigte Aluminum-Werke A.-G.). U. S. 2,211,681, Aug. 13, 1940 (Oct. 31, 1938).—In the manufacture of a highly reactive alumina, the process comprises continuously passing monobasic aluminum sulfite through two separate calcination zones, heating it indirectly with substantial exclusion of air in the first of the zones to temperatures sufficient to produce the evolution of the bulk of the SO_2 from the sulfite and collecting the SO_2 in substantially pure form, passing the resulting partially calcined sulfite into the second of the zones, heating it directly immediately before passing out of the zone to higher maximum temperatures not substantially exceeding 700°C. whereby the product is subjected to maximum furnace temperatures for a minimum period only without overfiring the resulting alumina, and collecting the evolved SO_2 admixed with combustion gases from the second zone.

Refractory cement. N. P. Pitt and Wilfred Gallay (Canadian Refractories, Ltd.). U. S. 2,210,327, Aug. 6, 1940 (Aug. 19, 1939).—A cement or mortar composition for laying up refractory brick, etc., comprises essentially finely divided particles of refractory material and a plasticizing agent consisting of an alkali-metal carbonate and dry particles of a partly expanded starch possessing the property that, when 6 gm. of it are intimately suspended and dispersed in 100 cc. of a 4% solution of the alkali-metal carbonate, it imparts to the resulting liquid suspension at 25°C. a viscosity substantially 20 or more times that of water.

Refractory investment. E. M. Prosen (Nobilium Products, Inc.). U. S. 2,209,035, July 23, 1940 (Nov. 26, 1938).—An investment material for use in casting an alloyed metal containing small amounts of finely divided periclase as well as monobasic ammonium phosphate and monobasic sodium phosphate in the ratio of substantially 3 to 1, a wetting agent of a dilute acid as temporary binder, and the remainder quartz proportioned in quantity and graded sizes whereby the investment thus has its coefficient of shrinkage controlled to equal substantially that of the metal being cast in the investment as the metal passes downwardly from the critical point at which the metal becomes rigid.

Terra Cotta

Borax-salt mixture improves appearance of salt-glazed ware. Anon. *Brick & Clay Record*, **95** [1] 30 (1939).—Borax used in the salting process improves the appearance of salt-glazed products. The borax may be either mixed with the salt or used separately. When used separately, it is added to the firebox just previous to the application of salt. Besides giving glazes of higher gloss, borax reduces the danger of crazing and, in some instances, permits salt

glazing at a lower temperature. Its successful usage in plants has been obtained by the trial-and-error method. Methods used by different plants are discussed. J.J.H.

Clay pit. C. GÜNTHER. *Tonind.-Ztg.*, **63** [48] 549–51 (1939).—Many failures and troubles in the manufacture of brick and roofing tile, such as variation in size, weight, and vitrification or cracking and bloating, are caused by faulty digging of the clay. The pit must be kept absolutely clean, and the different layers of clay should be dug uniformly and mixed thoroughly. W.K.

Errors in the production of pressed, grooved roofing tile. K. SPINGLER. *Tonind.-Ztg.*, **63** [38] 439–41; [41] 478–79 (1939).—For good results in the production of pressed roofing tile, a thorough preparation of the clay is necessary. The water content must be kept constant, scrap and new material should be mixed thoroughly, and the plaster molds should be uniform. W.K.

Processing clays for colors and surface effects. P. E. COX. *Brick & Clay Record*, **95** [1] 27–29 (1939).—The usual practice in applying glazes or clay slip coatings is to grind the coating in water and then dip the piece of ware in the tub of suspensions or apply the suspensions with a spray gun. An engobe, or slip, is a mixture of clays and fluxing minerals which may be colored or left in their natural state and which yield a surface on clayware. An engobe, when fired, makes a veneer. When a red-firing clay is applied as an engobe over a clay which fires another color, it is termed a red engobe or red slip. It is advisable to use a glue with the glaze or engobe. Heavy pieces of clay products, such as sanitary ware, terra cotta, and large electrical insulators, are generally finished with glazes mixed with glue. A detailed method of mixing glues with slip is described. For a salt glaze, common salt is mixed in a slip and applied in any convenient manner to the ware; the proportions should be about 35 salt to 100 parts by weight of slip material. A slip coating should be made up to fire light colored and should contain a considerable amount of potter's flint. The slip and salt mixture may be applied in one coat mixed with glue or sprayed on without glue. It should be fired in the usual manner; plants which usually cannot salt glaze will be able to if they fire to cone 1. Where the clays will not reach cone 1, owing to their nature, a mixture of salt and fluxes is necessary. A simple lead glaze would be better than the salt and clay slip in such cases. To obtain a manganese speckle, manganese dioxide is mixed with the slip material. Various materials are used for flashing the clayware in the kiln. Barium carbonate is helpful even though not needed because of scum. This applies particularly to vitrified ware. It is useless to attempt to flash until incipient vitrification is reached. The length of time of flashing depends on the clay. Flashed goods lose their flash in cooling if not cooled rapidly. Simple formulas are given. J.J.H.

Testing roofing tile for penetrability to water. E. ALBRECHT. *Tonind.-Ztg.*, **63** [36] 413–15; [37] 428–32 (1939).—To compare the quick and simple laboratory test for penetrability with the performance of tile on the roof, eleven roofing tile from various localities were subjected to natural and artificial rainfall for a number of years. Special attention was paid to the effect of the clogging of the pores. The duration of the rain is more important than the intensity. As a whole, laboratory tests give a fair indication of the quality of the product. W.K.

Whiteware

Ceramic insulators for spark plugs. FRANK H. RIDDLE. *S. A. E. Jour.*, **46**, 236–42 (1940).—R. reviews the composition and properties of clays, quartz, feldspar, porcelain, and spark-plug porcelain. Further work on spark-plug porcelain involves the replacing of quartz by zirconia, alumina, and titania. Satisfactory insulator bodies have been made from single compounds or oxides. New methods have been developed for forming nonplastic bodies. Properties involved in spark-plug performance are (1) porosity, which must be nearly zero so that permeability is virtually nil; (2) refractoriness, now satisfactory; (3) mechanical strength, several times that of porcelain tableware; (4) thermal expansion, lower than that of the metals in the spark plug so that clearance is needed for enclosed parts; (5) electrical resistance; magnesia and alumina are best, their resistance decreasing to 1 megohm per cc. at 850° to 1060°C.; (6) thermal conductivity, which determines plug temperature; (7) good resistance to thermal shocks; and (8) resistance to chemical agencies, especially tetraethyl lead; this burns to lead oxide, which reacts more readily with siliceous bodies than basic bodies. W.D.F.

Chemical ceramic ware. THEODORE R. OLIVE. *Chem. & Met. Eng.*, **46** [9] 512 (1939).—O. describes the plant processes used by the Lapp Insulator Co. in making chemical porcelain ware. The porcelain ware is made by slip casting, extrusion, and by a special lathe-cutting process. For extrusion purposes, a pugged clay obtained by filter-pressing a deaired clay slip is used, the resultant cake having a water content of 20% on the dry basis. The ware is fired in a tunnel kiln at a temperature above 2300°F. B.C.R.

Grinding: control of particle size in glaze slips. C. W. PARMELEE. *Ceram. Ind.*, **35** [1] 48–50 (1940).—P. believes certain enamel controls might advantageously be adapted to pottery glazes, viz., consistency, fine grinding, testing of specific gravity, and the relation between the absorption of the fired body and final results. A review of recent advances is included. L.M.C.

Materials for vacuum-tube manufacture. A. J. MONACK. *Ind. Eng. Chem.*, **32** [8] 1028–33 (1940).—Metals and alloys for use in glass-metal seals are enumerated. The various types of glass and other ceramic materials required are also discussed. Ceramic materials serve two purposes in vacuum tubes: (1) electrical insulation and (2) support and spacing of the tube electrodes. Electrical insulation is necessary both inside and outside of the tube (separation of lead wires in the base). Ceramics for use within the tube must have good strength, high purity (especially freedom from alkalis), good resistance to thermal shock, good refractoriness, and satisfactory electrical resistance, dielectric constant, and phase angle; ceramics used in bases must have low porosity and satisfactory electrical resistance. External ceramics are usually steatite bodies, and large quantities of these compositions are used internally. Where high temperature, high voltage, and high frequency act singly or in combination, insulators made of alumina, beryllia, magnesia, or mixtures of them with steatite must be employed. Fused quartz is sometimes used. Illustrated. F.G.H.

Shortcomings of mica insulation for aviation spark plugs. VAL CRONSTEDT. *S. A. E. Jour.*, **46**, 233–35 (1940).—In 5350 flying hours for 60 engines, scheduled replacement was 3500 and unscheduled 2187. Ceramic plugs were used satisfactorily in the last war, but later air-cooled engines had too high temperature fluctuations; the ceramic plugs cracked and eventually were abandoned. Mica was substituted. The most successful plug has lower washers of Canadian phlogopite and cigarettes of Brazilian lepidolite. Many designs have been tried, but it is still not satisfactory. Mica contains water which it loses at 1000° to 1200°F., and at operating temperatures it may approach or exceed this. It has a low heat conductivity and about half the thermal expansion of a stainless-steel electrode. Moisture collects on the mica washers when cold. Mica also reacts readily with the lead. It should be replaced by a more inert and stable material. W.D.F.

Shoulderless porcelain jacket crowns with reinforced platinum matrix. DANIEL STAPLES GARDNER. *Jour. Amer. Dental Assn.*, **26** [5] 744–53 (1939); *Met. Abs.*, **6** [7] 243 (1939).—The crowns are prepared by firing hard porcelain over a thin platinum cap the outer surface of which is covered with a thin 52-mesh gauze of 10% iridoplatinum, which serves as a reinforcement for the porcelain. The

gauze is soldered onto the cap with pure gold. The porcelain-coated cap is fixed to the prepared tooth by means of zinc phosphate cement in such a way that the cap extends about 1 mm. below the gingiva.

Symposium on substitution of American for imported clays in whiteware bodies: Introduction. ARTHUR S. WATTS. *Bull. Amer. Ceram. Soc.*, **19** [8] 281–82 (1940). **Properties of American kaolins and English china clays.** T. A. KLINEFELTER. *Ibid.*, pp. 282–83. **Discussion of paper by Klinefelter.** HEWITT WILSON ET AL. *Ibid.*, pp. 283–84. **Discussion on Norton studies.** J. R. BEAM ET AL. *Ibid.*, p. 284. **Discussion on Sproat studies.** LOUIS NAVIAS ET AL. *Ibid.*, pp. 284–85. **American ceramic materials in pottery.** HEWITT WILSON AND ERNEST WILSON. *Ibid.*, pp. 285–87. **Discussion of Wilson paper.** J. R. BEAM. *Ibid.*, p. 287. **All-American hotel china body.** G. A. LOOMIS AND W. H. EARHART. *Ibid.*, pp. 287–89. **Substitution of domestic clays for imported clays in electrical porcelain bodies.** L. E. THIESS. *Ibid.*, pp. 289–90.

BOOK

Historical Presentation of the Electrotechnique. History of the High-Tension Line Insulator (Historische Einzeldarstellungen aus der Elektrotechnik. Zur Geschichte des Freileitungs-Isolators). W. WEICKER, E. G. FISCHINGER, AND P. POSCHENRIEDER. Julius Springer, Berlin, 1932. 125 pp. Price 21 Rm. **Chapter I.** Translated by MAX M. MÜLLER.—Illustrations are described as follows: (1) Siemens insulator, 1850. (2) Borggreve insulator, 1857, proved impractical due to its square-shaped hole. (3) Commission insulator, 1857, a glass insulator developed by a special commission appointed by the chamber of commerce of Prussia. (4) Double-bell porcelain insulator, 1858, developed by Chauvin, Director in Chief of the Prussian telegraph system; this type was introduced in most countries in various shapes. (5) Various types of 4. The same design was made the standard model for telegraph lines in Prussia in 1862 and is still used, except for a few minor alterations; three standard types have grown from that model, viz., RI, RII, and RIII; the Roman figures specify the sizes, RI 5.6 in., RII 4 in., and RIII 3.2 in. This insulator was used even for power lines; especially in the southern part of Germany. In 1920 and 1922, however, the VDE (Society of German Engineers) standardized special models for that purpose, viz., N60, N80, and N95. (7) Insulator made according to a patent of Lenoir and Prudhomme, 1869; it is considered to have been the precedent of the oil insulator. (8) Oil insulator patented by the English telegraph engineers Jackson and Philipps, 1876. (9) A two-piece insulator mentioned in a German patent taken out under the name of patent-attorney Pieper in 1877. In 1886 oil insulators were used for the first time to carry a high-power line. The Oerlikon Mfg. Co. (Switzerland) used them successfully for a voltage of 2000 volts. It was not until 1891, however, that oil insulators were recognized as high-tension insulators. The occasion was the Electrotechnical Exposition at Frankfort on the Main when the famous power line from Frankfort to Lauffen on the Neckar was switched into operation; the tension was 15 kv. but later on the line was successfully tried at 30 kv. One of the poles employed and the two types of insulators used are illustrated (10, 11, and 12). After a period of time the line failed, for the insulators ceased to be insulators. The oil had been contaminated by dust and dead insects; furthermore, it had crept over the surface of the porcelain, and the insulator was covered with a thin film of oil. Three hundred of those oil insulators, however, were later used in a 15-kv. power line near Oerlikon where they were kept in use until 1900.

In Italy also, the oil insulator found application in a high-tension line; in 1892 a 5-kv. line was built from Rome to Tivoli. The insulators were of the type shown in Figure 14, and they were not replaced until 1903; during the last 4 years the line was operated at 10 kv., and short circuits occurred frequently. A number of high-tension lines were equipped with oil insulators during the nineties; they very rarely were filled with oil but were used dry. About 1895 a 3-shell (3-bell) type insulator began to replace the oil insulator. Figure 15 shows one of the early types. This type was used especially in Switzerland and Germany. It worked satisfactorily on wooden poles for voltages up to 20 kv. A higher voltage required insulators of a size which at that time was too difficult to manufacture.

Figure 16 shows the Paderno insulator developed by the Richard Ginori Porcelain Co., Milan, in 1896. In 1897 R. M. Friese in connection with O. Arke, director of the Hermsdorf Porcelain Co., developed the Delta insulator, which represents a milestone in the history of electrical insulators. (17, 18) Earliest forms of the Delta type. An improvement on this type was the abandonment of the idea of a one-piece insulator; two pieces were joined during firing by means of a glaze which was applied to the joint surfaces. (21) Two-piece Delta insulator used in 1904 on a 40-kv. line. (22) Delta insulator, 1907. (23) Delta insulator, 1917. (24) Delta insulator, 1920, standard type. About 1905 the parts of a Delta insulator were fired separately and then joined. A litharge-glycerine was used as a cement, but it caused cracking; other cements were tried but did not give satisfactory results. In 1915 a good bond was developed in the form of a graphite-sodium silicate coating covered with an elastic lacquer. In 1922 the one-piece insulator was again widely used; the two-piece type underwent further improvements, however, which consisted mainly of new means of bonding, including screws and clamps instead of cements. In spite of the fact that the Delta insulator predominated the field, other designs were developed which found use in industry.

Figures 25 and 26 show the Groove insulator, 1905, and the Kammer insulator, 1906, both by the Ph. Rosenthal Inc. Porcelain Mfg. Co. (27) Two-shell insulator by G. Benischke, 1910. (28) Groove-plate insulator by Siemens and Halske, 1902. (30) Betznan insulator, by the Ginori Porcelain Co., 1905; used especially in Switzerland. The two pieces touched each other on a small shoulder only, leaving an air space between the upper bells. The bond was a glaze. (31) Italian insulator, glazed together. (32) American glass insulator, used in 1898 on a 40-kv. line in Provo, Utah. (33–36) Older American porcelain insulators. (37) American insulator, 1919. (38) A newer type of American insulator. (39) Faradaid insulator by the Westinghouse Electric & Mfg. Co., 1918. (40) Wide-rim insulator by the H. Schornling and Sons Porcelain Mfg. Co., Inc., 1921. This wide-rim (*Weitschirm*) type is the Faradaid insulator as adapted by the above-mentioned company. It proved to be so successful that in 1929 it was standardized in addition to the Delta insulator, which had been standardized in 1920. In 1910, W. Weickert proposed a metal-rim type, which was used in a 60-kv. line between Desson and Bitterfeld. A very similar type was also developed in 1910 by Nicholson and employed in a 60-kv. line from Buffalo to Syracuse, N. Y. Figure 41 shows this type. (42) Reinforced Delta insulator by Siebert, Kassel, 1925. (43, 44) German standard types, standardized in 1929. (45) Solidly supporting insulator by AEG, 1924. (46) American insulator by Imlay and Thomas, 1912.

In Scandinavia and other places, queer atmospheric conditions in addition to a strongly salty sea air caused ordinary insulator types to fail in a very short time. In an effort to overcome this disadvantage, the Swedish Royal Waterfall Department developed a salt-proved type (47).

Another insulator for withstanding severe weather conditions is the fog-pin type developed by the Lapp Insulator Co. (48).

PATENTS

Aviation spark plug. JULIUS DEVINE. U. S. 2,208,667, July 22, 1940 (Aug. 15, 1939). U. S. 2,208,668, July 23, 1940 (Feb. 16, 1940).

Glazing ceramic ware. B. A. JEFFERY (Champion Spark Plug Co.). U. S. 2,209,624, July 30, 1940 (Aug. 5.

1937).—The method consists in forming a ceramic slip, spray-drying the slip into a powder composed of tiny rounded pellets, filling the powder into a cavity of predetermined shape, compressing the powder in the cavity, by hydrostatic pressure, into a shaped article, suspending glazing material in a liquid that does not develop the colloidal properties of ceramic material, applying the suspension to the surface of the article, and firing the coated article.

Saucer. R. G. COWAN (Onondaga Pottery Co.). U. S. 2,210,283, Aug. 6, 1940 (Oct. 20, 1938).

Spark plug. A. C. HASTINGS, JR. Can. 388,758, May 21, 1940 (Jan. 20, 1939; in U. S. Feb. 11, 1938). G.M.H.

Spark plug. F. D. SPRAGUE (Sprague Specialties Co.). U. S. 2,208,708, July 23, 1940 (June 2, 1939).

Spark plug for internal combustion engines. J. C. CARTER. U. S. 2,209,621, July 30, 1940 (Jan. 24, 1940).

Water closet. SVEN DUNER (Duner Co.). U. S. 2,210,630, Aug. 6, 1940 (Aug. 15, 1938).

Equipment and Apparatus

Automatic control of vacuum pumps. ANON. *Tonind.-Ztg.*, **62** [83] 933–34 (1938).—A simple electric device is described which indicates interruption of the vacuum in deairing machines by a red light. W.K.

Construction of deairing extruding machines according to patent literature. G. HELM. *Tonind.-Ztg.*, **63** [39] 451–53; [40] 464–65; [42–43] 488–90 (1939).—H. discusses the development of the vacuum press and the different solutions of the problems encountered as shown in American, German, Austrian, English, and Swiss patents. W.K.

Deairing machines in roofing tile plants. A. C. HEIL. *Tonind.-Ztg.*, **62** [35] 396–97 (1938).—The two augers must be adjusted to pass the same amount of material. For this purpose, the perforated plates should be adjustable or exchangeable. W.K.

Experimental work on the development of the electron microscope. L. C. MARTIN, D. H. PARNUM, AND G. S. SPEAK. *Jour. Roy. Microscopical Soc.*, **59** [4] 203–16 (1939).—A beam of electrons, derived from a cold-cathode discharge tube, passes through a small anode hole (0.1 mm.) into the main tube, which represents the microscope proper, and traverses in succession three coils which have functions analogous to those of the condenser, objective, and projection lens of a photomicrographic apparatus. Fluorescent screens or photographic plates register the image at either the first stage or the second stage of magnification. A general diagram of the arrangement is shown. Descriptions and diagrams of the electrical supply are given. Possible causes of residual defects are outlined. New fittings and their use and a new procedure for centration are included. G.R.S.

Explosives in safekeeping. C. H. FISHER. *Mining Congr. Jour.*, **26** [6] 14–15 (1940).—Explosives should be protected from moisture, the weather, fire, excessive heat, and theft. The proper distance of a barricaded magazine from other buildings is given in the American Table of Distances. The barricade should be 3 ft. of earth, not stone, as the stone would become missiles in an explosion. For permanent use a brick magazine is best, with medium soft brick. Sand-filled magazines are also used. Metal buildings for temporary use should be bulletproofed. The magazine should be ventilated. In use, the safety rules should be followed carefully. Blasting caps should never be stored in the same magazine with the explosives. W.D.F.

Field emission microscope. M. BENJAMIN. *Jour. Soc. Glass Tech.*, **24** [102] 93–96 (1940).—A brief description is given of a simple projection-type electron microscope which operates by extracting electrons from a fine point by means of a concentrated electric field. The patterns produced on a fluorescent screen by various clean and contaminated metals are illustrated. G.R.S.

Hard-facing for modernization. R. L. LERCH. *Mining Congr. Jour.*, **26** [6] 16 (1940).—Hard-facing reduces the time equipment stands idle, as it outwears plain steel 3 to 10 times. It is best to hard-face new parts when placed in service. Only welding equipment and a supply of the correct rods are needed. Gyratory and jaw crushers, bucket lips, conveyer-belt clips, and many other parts are hard-faced successfully. W.D.F.

Heat insulation on cylindrical surfaces. CHANNING TURNER. *Ind. Eng. Chem.*, **32** [7] 904–906 (1940).—A graph is presented for the rapid calculation of heat transfer by correlation of the relative effectiveness of insulation with its thickness and radius of curvature, as defined by the ratio of diameter of cylinder to diameter of insulation. Illustrated. F.G.H.

High temperature laboratory furnaces. M. PIRANI. *Jour. Sci. Instruments*, **17** [5] 112–15 (1940).—P. describes the construction of two types of laboratory furnaces for temperatures up to 1900°C. One furnace employs beryllium oxide as the refractory and a molybdenum heater. The other uses zirconium silicate refractories. Both units must operate in a hydrogen atmosphere to protect the molybdenum windings from oxidation. 6 figures. J.L.G.

Increase of the light intensity of optical instruments. A. SMAKULA. *Z. Instrumentenk.*, **60** [2] 33–36 (1940).—The light intensity of optical instruments depends on the reflection of the light on the boundary surfaces between glass and air as well as on the absorption of light in the glass; the absorption is almost negligible in the visible range, being only about 1 to 2% for white light for each 1-cm. length of glass. The reflection causes a greater reduction in intensity and also impairs the contrasts in the picture; the loss by reflection for a glass with a refractive index of 1.50 and an angle of incidence equal to 0° is as follows:

Number of reflection surfaces	2	4	6	8	10	12
Loss by reflection (%)	7.8	15.0	21.7	27.8	33.5	38.7

The losses by reflection depend on (1) wave length of light, (2) angle of incidence of the light rays, (3) refractive index of the glass, and (4) the number of boundary surfaces between glass and air. Efforts have been made to eliminate reflection by chemical and physical means. The former consists in etching the glass surface with acids, e.g., $H_2S_9(NH_4)_2S$, etc., which dissolve one or more constituents out of the glass so that a layer remains with a refractive index smaller than that of the glass. Glasses with high SiO_2 content, however, cannot be treated in this manner, and this method has not found practical application. The physical process of producing a thin layer of smaller refractive index (condition for elimination of reflection) consists in depositing it on the glass, preferably by evaporating a liquid of low refractive index on the glass surface; the amplitude and phase of the incident light and the thickness of the layer, however, must be in a definite ratio for good results. In this case, if reflection is reduced to 0.5%, the loss is as follows:

Number of reflection surfaces	2	4	6	8	10	12
Loss by reflection (%)	1.0	2.0	3.0	3.9	4.9	5.9

The effect of the reduction or elimination of reflection is shown in photographs taken with reflecting and reflection-free objectives. The formulas for determining amplitude and phase conditions are given. M.H.

Infrared lamp banks for drying finishes and materials. ANON. *Product Eng.*, **11** [7] 307–10 (1940).—Radiant energy in the infrared range is now produced by tungsten lamps of 500- and 1000-watt capacity which emit about

90% of their input as infrared energy; the maximum energy distribution occurs at about 11,000 to 14,000 a.u. (0.0000011 to 0.0000014 m. wave length). Installations for drying small painted and enameled parts are described. The reflectivity of the material to be dried is important; the higher the reflectivity, the less energy is absorbed and the longer is the drying time. The reflectivity of some pigments is as follows:

Pigment	Wave length (a. u.) 6000	9500	44,000
Cobaltic oxide (steel gray)	3	4	14
Chromic oxide (dark green)	27	45	33
Lead oxide (yellow)	52		51
Ferric oxide (red)	26	41	30
Lead chromate (yellow)	70		41
Zinc oxide (white)	82	86	8
Lead carbonate (white)	88	93	29

The fast-drying enamels best suited for lamp drying are made with short oil modified alkyd (glycerol phthalate) resins which may be further modified with urea-formaldehyde resins if greater hardness is desired. If high enough intensities are available, nondrying alkyd and urea-formaldehyde combinations are useful. One advantage of infrared heating over air or oven drying is that heat is instantly available with the lamps, whereas some time is required to bring the oven and parts up to working temperature. Drying time can sometimes be cut to one fourth the time of oven drying. A number of applications is compiled with comments on practicability. This method is compared with other drying methods. M.H.

Machinery for winning raw materials in brick plants. W. KOSNEY. *Tonind.-Ztg.*, **62** [81] 907–10; [82] 919–21 (1938).—Machines and power tools for the winning and transporting of clay, such as scrapers, shovels, compressed-air tools, tractors, and transport cars, are discussed, and their uses are recommended. Illustrated. W.K.

Machines in ceramic production. F. LIPINSKI. *Tonind.-Ztg.*, **62** [74–75] 827–40 (1938).—Machines for mining, hauling, storing, aging, preparing, and all kinds of forming are discussed and illustrated. W.K.

Mercury recording thermometer for use over long periods of time. L. O. COOK. *Jour. Sci. Instruments*, **17** [6] 161–62 (1940).—The record is obtained by casting the shadow of a flat section mercury column of a thermometer on bromide paper or film from a feeble source of light. The recorder is actuated by a constant clock with an intermediate mercury-in-glass type switch operating a relay which drives the drums carrying the paper. The thermometer is graduated in half degrees. A tenth is easily estimated. 3 figures. J.L.G.

New spectrograph testing technique established at Pearl Harbor Navy Yard. W. H. HAMMOND. *Jour. Amer. Soc. Naval Engrs.*, **52** [1] 65–76 (1940); abstracted in *Bull. Brit. Non-Ferrous Metals Research Assn.*, No. 131, p. 125 (1940).—A grating spectrograph has recently been installed in the general testing laboratory, and applications and limitations of arc methods are described. Special film-processing equipment with temperature control for rapid working is also described.

Optics of the electron microscope. L. C. MARTIN. *Jour. Roy. Microscopical Soc.*, **59** [4] 217–31 (1939).—Grosser image defects are ascribed to chromatic aberation combined with centering error. This can be minimized by (*a*) improving the centering and symmetry of the objective coil as far as possible, (*b*) improving the homogeneity of the beam, and (*c*) controlling the region of the first-stage picture projected by the second-stage lens. Not until the chromatic error has been removed as far as possible can the disturbances due to other causes mentioned above be investigated. G.R.S.

Particle-size determination of colloidal systems by the supercentrifuge. E. A. HAUSER AND H. K. SCHACHMAN. *Jour. Phys. Chem.*, **44**, 584 (1940).—A method of calculating the particle size of a suspension from data obtained with the Sharples ultracentrifuge is described. R.A.G.

Photoelasticity—mining engineer's new tool. ANON. *Mining & Met.*, **21** [398] 94 (1940).—Photoelastic stress analysis has become a powerful tool to the designing engineer during the past few years because complex structures can be studied with inexpensive models that can be easily modified until the best design is developed. An important result from this method is that optimum safety is assured; when a piece of isotropic transparent material, such as glass, celluloid, or Bakelite, is stressed and viewed in polarized light, the picture seen indicates by its color bands of light or fringes places where dangerous stress concentrations occur. Stresses in a mine pillar vary greatly and are influenced to a considerable degree by the load, the deflection of the strata over it, and its shape; stresses in openings and the intervening strata under pillars vary greatly and are determined by the pillar load and the relative positions of opening and pillar bottom. Combined barodynamic photoelastic methods offer a means of determining the values, direction, and distribution of these stresses. The application of these methods should result in safer workings and in lower maintenance costs. J.J.H.

Present position of development of the electron microscope. L. C. MARTIN. *Jour. Soc. Glass Tech.*, **24** [102] 97–100T (1940).—M. classifies the types of electron microscopes and comments on their nomenclature. The possibilities and developments of such apparatus are outlined. G.R.S.

Progress in ball-mill design: I. D. W. RUDORFF. *Eng. & Boiler House Rev.*, **54** [1] 8 (1940).—Optimum ball-mill speed is influenced by such factors as diameter of the barrel, size of balls, shape of barrel lining, and resistance of the material to grinding. In general, a speed of 75% of the critical is advocated, although speeds of 50 to 60% are recommended when the mill is filled 40% full of balls. The critical speed is that at which the balls are forced against the inner lining by centrifugal force. Although the use of balls of several diameters is usually recommended, an exhaustive study made of a Hardinge mill used for grinding coal indicated that a uniform charge of 30-mm. balls was preferable to the manufacturer's recommendation of 50% of 40-mm. and 50% of 70-mm. balls and to either 40-mm. or 50-mm. balls. The use of 30-mm. balls resulted in lower power consumption (weight of ball charge was correspondingly less), finer grinding, and greater mill capacity. It should be noted that the use of balls of only one size limits the particle sizes obtainable. In comparing the grinding characteristics of 30-mm. and 40-mm. balls, R. concludes that the smaller balls tend to reduce the amount of extremely fine material, 0 to 10 microns, and increase the 15 to 30-micron sizes. B.C.R.

Psychrometric chart, application and theory: XIV. WILLIAM GOODMAN. *Heating, Piping & Air Conditioning*, **12** [7] 431–33 (1940).—Appendix 8, containing derivations of equations given in earlier articles, is presented. Two tables. For Parts **XII** and **XIII** see *Ceram. Abs.*, **19** [9] 220 (1940). J.L.G.

Pumping abrasive solids in suspension. J. C. FARRANT. *Mech. World & Eng. Record*, **107** [2784] 407–408 (1940).—The parts of a pump for abrasive solids exposed to abrasion are usually made of ordinary cast iron, white iron, or manganese steel. F. describes a pump in which the metal surfaces of the pumping parts are covered with abrasion-resisting rubber. Life of the rubber-protected parts is claimed to be 25 times that of unprotected metal. Illustrated. F.E.S.

Quartz crystals. Their piezoelectric properties and use in control of high frequencies: II, Nature of quartz and manufacture of crystals. C. F. BALDWIN. *Gen. Elec. Rev.*, **43** [6] 237–43 (1940).—The raw material or "mother quartz," its properties and deposits, and the methods of manufacture of crystals are described. Holders or mountings, cutting machines, and other apparatus for lapping crystals to a high precision are shown. 6 illustrations. For Part I see *Ceram. Abs.*, **19** [8] 195 (1940). L.E.T.

Rock breaker. IOWA MFG. CO. *Roads & Streets*, **83** [6] 97 (1940).—This slow-speed fixed-bar breaker pro-

duces a uniform cubical product in any size required by simple variations of speed. P.G.H.

Self-regulation of resistance furnaces for high temperatures [Stratit furnaces]. A. VON ENGEL. *Bull. Assn. Suisse Élect.*, **30**, 162–66 (1939); *Science Abs.–B*, **42**, 217 (1939); *Met. Abs.*, **6** [11] 482 (1939).—"Stratit" heating elements consist of molybdenum bars embedded in vacuum-tight ceramic tubes, the ends of the bars being water cooled. Self-regulation of the furnace temperature takes place to some extent when resistances of this character are used, as they have a positive temperature coefficient.

Sensitive method for determination of moisture, applied to electrical insulation materials. R. S. VINCENT AND A. SIMONS. *Proc. Phys. Soc.* [London], **52** [292] 489–500 (1940).—A method is described for measuring the adsorbed moisture in paper (or other insulation materials) down to values of 0.01%. The essential feature of this method is the establishment of the equilibrium water-vapor pressure of the sample at a chosen temperature in a known space. A new form of absorption apparatus is employed to measure the equilibrium water-vapor pressure, and from such measurements the original total adsorbed moisture of the sample is derived by means of a simple graphical extrapolation. A picture of the apparatus and four diagrams are presented. L.E.T.

Thermal conductivity sliding graph. J. E. PLUCK. *Eng. & Boiler House Rev.*, **54** [1] 14 (1940).—P. describes in detail the construction of a calculator for determining the thermal conductivity of furnace walls constructed of several types of materials, such as refractory insulating and building brick. Calculations that would otherwise require several hours may be made in several minutes. B.C.R.

Wear and size distribution of grinding balls. FRED C. BOND. *Amer. Inst. Mining Met. Engrs. Tech. Pub.*, No. 1191; *Mining Tech.*, **4** [3] 12 pp. (1940).—B. determines the size distribution of the equilibrium ball charge in the mill. This should be approximated as nearly as possible in the initial ball charge. Increase in ball size will give a decrease in the ball weight lost by grinding. This does not affect the surface area produced but does produce more fine and more coarse particles. Except in the cement industry, the object of grinding is to obtain particles which will pass a certain mesh; the production of much finer particles is unwanted and may be detrimental. The best conditions are (1) use of a circulating load, (2) short detention time, and (3) adjustment of ball sizes so that the largest breaks the largest particles in the feed; the size distribution of the balls and of the material should correspond. For any set of conditions, there is a minimum difference in the size number of a particle and that of the ball required to break it which is constant for all sizes. This ranges from 4 to 9. The size distribution of the equilibrium ball charge and, from this, the size distribution of the ball feed are calculated. Closed-circuit operation returns a large amount of material finer than the new feed and makes it advisable to include small balls in a mill feed. Calculations on an actual mill with a circulating load and new particle feed up to 1 in. showed the best ball feed to be 70% 5 in. and 30% 2 in. W.D.F.

Wire conveyer belts in the glass industry. GEORG DROST. *Sprechsaal*, **73** [19] 163–66 (1940).—Wire-netting, spiral-link, and flat and round wire belts, varieties of mesh, and the construction of belts used in glass plants for conveying objects in annealing furnaces, etc., are compared to give the technician criteria for judging and selecting the most suitable types. Wire-net belts facilitate the penetration of heat and are advantageous in regard to weight. M.V.C.

PATENTS

Apparatus for the manufacture of hollow and indented dry-pressed ceramic ware. BENJAMIN LASSMAN (Hydraulics, Inc.). U. S. 2,209,404, July 30, 1940 (July 6, 1937).—Apparatus for forming articles from granular material, etc., into ware in which there is a cavity.

Cement cooler. J. E. CURTIS (Cowham Engineering Co.). U. S. 2,209,561, July 30, 1940 (Aug. 17, 1938).

Clay blunging and decolorizing apparatus. S. C. LYONS (Bird Machine Co.). Can. 389,415, June 18, 1940 (May 7, 1938; in U. S. May 8, 1937). G.M.H.

Machine for classifying fine-grained materials. A. D. SINDEN. U. S. 2,210,505, Aug. 6, 1940 (July 11, 1938).

Production of dry granulated slag. TRACY BARTHOLOMEW. U. S. 2,210,999, Aug. 13, 1940 (Dec. 20, 1937).

Sand washing and grading apparatus. HARRY A. STELLEY. Can. 389,553, June 25, 1940 (Feb. 11, 1938; in U. S. May 15, 1937). G.M.H.

Kilns, Furnaces, Fuels, and Combustion

Automatic stoker for periodic kilns. J. GREWE. *Tonind.-Ztg.*, **63** [37] 425–28 (1939).—Automatic stokers effect a more uniform firing and a saving in man power. Arrangements for their use on periodic kilns are sketched and discussed. W.K.

Burning coke breeze on chain-grate stokers of water-tube boilers. ANON. *Coke*, **1**, 203–205 (1939); *Brit. Chem. & Phys. Abs.–B*, **59** [4] 252 (1940).—Satisfactory tests carried out at Fulham Gasworks are described.

Economies of combustion control in industrial ceramics. R. C. HUTCHISON. *Bull. Amer. Ceram. Soc.*, **19** [8] 295–98 (1940).

Factors affecting flame velocity. D. T. A. TOWNEND AND M. MACCORMAC. *Engineering*, **149** [3861] 45 (1940).—Among the factors which have led to the abandonment of the Mallard and Le Châtelier theories of flame propagation and the Arrhenius theory of activation of energy are (1) the disproportionate influence of inhibitors such as water vapor, NO_2, and tetraethyl lead, (2) the acceleration of slow combustion by inert gases, and (3) the abrupt transition with some change in experimental pressure or temperature from an immeasurably slow reaction to spontaneous ignition and vice versa. The contributing factors to flame propagation are (*a*) rising temperature due to conduction of heat from the flame front, (*b*) actual diffusion of centers from the flame front, and (*c*) the presence of promoters in the explosive mixture. Present knowledge does not permit any assessment of the relative importance of these factors. B.C.R.

Heat from kiln walls. W. GIECHE. *Tonind.-Ztg.*, **63** [50] 572–74 (1939).—The idea of recovering some of the heat apparently lost in the walls and floor of a ring kiln is tempting. The cost of installing air ducts is high, however, and the coefficient of heat transfer is so low that the results are unsatisfactory. Heat cannot be removed from a kiln under fire without additional consumption of fuel. W.K.

Influence of position in the kiln on the resistance to freezing of brick and roof tile. H. ROTH. *Tonind.-Ztg.*, **63** [52] 595–96 (1939).—Ring kilns and zigzag kilns often show wide differences in temperature during firing between the top and the bottom and, on drawing, between the ends of the chamber. These differences influence the resistance to freezing. With proper attention, the firing can be equalized and the product made more uniform. W.K.

Kiln doorway closure. A. MÖSER. *Tonind.-Ztg.*, **64** [1] 2–4 (1940).—Instead of the old-fashioned, wasteful method of closing kiln doorways by piling up brick, M. suggests various improvements, e.g., recessing the doorway, making it rectangular instead of semicircular, and using refractory concrete. Another solution is a door comprising an outer and an inner panel; the space between the panels is filled with sand, and the door is opened and closed by raising and lowering it. The use of a door unit made from insulating firebrick is discussed. Illustrated. F.E.S.

Plastic properties of bituminous coking coals. Effect of oxidation. R. E. BREWER, C. R. HOLMES, AND J. D.

DAVIS. *Ind. Eng. Chem.*, **32** [7] 930–34 (1940).—Illustrated. See *Ceram. Abs.*, **19** [8] 197 (1940). F.G.H.

Practical working of tunnel kilns. A. RITTGEN. *Ber. Deut. Keram. Ges.*, **20** [3] 131–43 (1939).—R. emphasizes the need for tunnel kilns in every modern ceramic plant and their advantages over other types in regard to firing time, consumption of fuel, and fast delivery service. Three kinds of tunnel kilns are used: those fired with generator gas, those fired with distributed gas, and electric tunnel kilns. The principles on which these kilns work are described. Comparative data show the fuel consumption of tunnel kilns and box-type kilns. Various plants which have special problems to overcome are described. Tunnel kilns constructed in 1906 by Tielsch, Altwasser, are still working. A comparison between gas-fired and electric kilns is given. Tunnel and box-type kilns used by the Reichwerke Hermann Göring, Schwarzenfeld, Bavaria, are fired with generator gas obtained from vaporized raw lignite. The safety of tunnel kilns fired with distributed gas is discussed. An example is given of an economical calculation for a gas-fired or electric tunnel kiln. W.D.K.

Tunnel kiln for brick firing. N. LENGERSDORFF. *Tonind.-Ztg.*, **63** [42–43] 490–93 (1939).—The gas-fired tunnel kiln should be adopted more widely for firing brick because it (1) improves greatly the working conditions for the setting and drawing crew as well as for the firemen, (2) it is the best possible solution for the problem of ceramic firing, (3) the fuel and the waste heat can be used most effectively, and (4) the quality of the product can be controlled more closely. W.K.

BOOK

Fuel Flue Gases. Application and Interpretation of Gas Analyses and Tests. Edited by C. GEORGE SEGELER. Prepared under the auspices of the Chemical Committee, American Gas Assn. American Gas Assn., New York, 1940. 198 pp. Price $5. Reviewed in *Ind. Eng. Chem., News Ed.*, **18** [15] 673 (1940). F.G.H.

PATENTS

Burners and fittings for radiant-tube furnaces, etc. SANDERSON BROS. & NEWBOLD, LTD., AND J. G. HOLMES. Brit. 523,432, July 24, 1940 (Jan. 6, 1939).

Kiln. J. T. ROBSON AND G. R. SYLVESTER (Ferro Enamel Corp.). Can. 389,151, June 4, 1940 (April 3 1937; in U. S. Feb. 4, 1937). G.M.H.

Pottery support for glaze firing. A. L. SCHREIBER. U. S. 2,208,734, July 23, 1940 (May 3, 1938).

Geology

Association of magnesia with silica in a pure magnesium clay. P. G. NUTTING. *Jour. Wash. Acad. Sciences*, **30**, 233–37 (1940).—The white Hector clay described by Foshag and Woodford (*Ceram. Abs.*, **15** [6] 188 (1936)) breaks down in hot acid solutions, but at markedly lower acid concentrations than the swelling Wyoming bentonite. The curve showing the relation between the acid concentration and the pH of the filtrate lies higher than that for seven other clays and shows a pronounced shoulder in the intermediate acid range not shown by others. The presence of this shoulder indicates that hydrogen ions are inactivated either by physical adsorption or by chemical reaction or that hydroxyl ions are released in this range. J.B.A.

Base-exchange capacity determination of soils, etc., using the colorimetric manganese method. C. A. BOWER AND EMIL TRUOG. *Ind. Eng. Chem., Anal. Ed.*, **12** [7] 411–13 (1940).—A rapid and accurate colorimetric method for the determination of the base-exchange capacity of soils, clay minerals, etc., has been developed which involves saturation with divalent manganese by treatment with manganous chloride solutions. After displacement, the manganese is oxidized to permanganic acid and determined colorimetrically. Color comparisons are conveniently made by means of either Nessler tubes or a photoelectric colorimeter. Comparative results obtained involving saturation with calcium and manganese are in good agreement. Complete saturation with manganese is easily effected, since hydrogen and other common cations are readily displaced by manganese. Moreover, the method is sensitive and well adapted for micro work. F.G.H.

Clay sheets from bentonitic slips. ERNST A. HAUSER. Read before the Technical Association of the Pulp and Paper Industry, New York, 1939; abstracted in *Ceram. Ind.*, **35** [2] 58, 60 (1940).—Observations on the strength of clays as a function of particle size and on base exchange, described in connection with a method of making paper from bentonitic clays, are of interest to pottery manufacturers. Illustrated. L.M.C.

Clays and fuller's earth: V. F. SCHWARZ. *Sprechsaal*, **73** [20] 173–75 (1940).—Neutralization of NaOH-HCl buffered with clay substances yielded definite phenomena and conclusions. Previous experiments had been made with acid-base indicators. In this case the same experiments were repeated electrometrically for greater accuracy and to obtain a better picture of the buffering qualities of clays. The mode of experimental procedure is explained, and equations for calculating the electropotential and the pH are given. Neutralization with buffering additions of different clay substances, (1) air-dried and (2) heated, was carried out. Data are tabulated, and "buffer" curves for kaolin, fuller's earth, and ball clay are plotted. The differences of clay substances were determined from the results of the potentiometric investigations, and conclusions on the natural origin of the clays and their behavior and technological qualifications were drawn. The air-dried kaolin used had little power to change the base-acid neutralization, but when calcined to 770° it became much more active in comparison with the other clay samples. From the buffer curve (as from the Debye-Scherrer diagram), a change in the lattice structure of the clay substance can be determined. This is of importance in supervising the finishing firing of white earthenware and the convertibility of kaolin (production of alumina). The fuller's earth showed no difference in buffering action when air-dried or when heated to 125°. Maximum activity was reached at 425°, but this result does not necessarily apply to other fuller's earths. At 530° and 770° activity decreased. A slight similarity between the kaolin and fuller's earth curves at 770° suggests that the lattice of the latter might be destroyed at this temperature. The ball clay behaved like the fuller's earth in the air-dried state and at 125°; at 425° it reacted like the kaolin, and at 530° it appeared unstable. The buffering action of this clay when heated corresponds to its technological behavior: great plasticity, shrinkage on drying, thixotropy, suitability for engobe and thick wash, and low sintering point. For Part IV see *Ceram. Abs.*, **18** [10] 278 (1939). M.V.C.

Composition and properties of superphosphate. H. L. MARSHALL AND W. L. HILL. *Ind. Eng. Chem.*, **32** [8] 1128–35 (1940).—Suitable reference systems for the graphical comparison of the distributions of phosphorus among the principal forms in widely different superphosphates are discussed. The comparison is based primarily on the degree of acidulation, which is expressed quantitatively by a coefficient of acidulation or corrected acid-rock ratio, and takes into account the acid consumed by the aluminum and iron as well as the acid value of the fluorine in the superphosphate. A procedure is outlined for the interpolation of the acid requirements of phosphate rock which will be useful to superphosphate manufacturers interested in the greatest possible acid economy. The range of the degree of acidulation used in commercial practice is estimated from plant data and from the analyses of commercially prepared superphosphates. Illustrated. F.G.H.

Fluorspar, its chemical and industrial applications. LENHER SCHWERIN. *Jour. Chem. Education*, **17** [4] 160–65 (1940).—S. briefly outlines the history, properties, ec-

currences, and uses of fluorspar. A new and rapid method for the chemical analysis of fluorspar is proposed.
P.G.H.

Industrial minerals of Canada in 1939. L. H. COLE. *Can. Mining & Met. Bull.*, No. 338, pp. 281–94 (1940).—C. discusses 28 industrial minerals. An excellent bentonite at Rockglen, Sask., is being investigated. Feldspar production declined during the year, largely due to competition with nepheline syenite, the production of which is likely to continue to increase. A mill has been built in the Madoc, Ont., district for the recovery of fluorspar by concentration of old waste dumps. Magnesitic dolomite is quarried in Quebec; its use in refractory materials continues to expand. Deposits of brucite in Ontario and Quebec are being investigated. The Canadian silica industry continues to expand.
G.M.H.

Kaolin and some Belgian clays. W. DE KEYSER. *Ann. Mines Belgique Special Reprint*, 1939; *Trans. Brit. Ceram. Soc.*, **39** [5] 41A (1940); *Ber. Deut. Keram. Ges.*; **21** [2] 29–51 (1940).—(1) Zettlitz kaolin, (2) pure Belgian clays (plastic), and (3) common clays, were studied to determine their behavior under heat treatment. Kaolin can be dehydrated by heating in vacuum at 300°, but this may not be the lower limit, since prolonged heating and repeated crushing increase the loss of water. This is in support of the theory that the H_2O is in solid solution in kaolin. A study of the dielectric constant showed that the H_2O:-Al_2O_3 ratio is 1.75; hence, the formula of clay substance should be $2SiO_2 \cdot Al_2O_3 \cdot 1.75H_2O$ and not $2SiO_2 \cdot Al_2O_3 \cdot 2H_2O$. The following conclusions are drawn from the results of the work: metakaolin, $2SiO_2 \cdot Al_2O_3$, is formed after dehydration; this decomposes between 800° and 830°; from 830° to 910° dissociation of metakaolin continues, with the formation of γ-Al_2O_3; from 910° to 975° sillimanite is formed, and above 975° mullite is formed. See *Ceram. Abs.*, **19** [3] 75 (1940).

Progressive metamorphism of siliceous limestone and dolomite. NORMAN L. BOWEN. *Jour. Geol.*, **48** [3] 225–74 (1940).—The metamorphism of siliceous dolomitic limestone is considered with the aid of a composition tetrahedron which suggests that the changes may be referred to thirteen steps or grades of increasing decarbonization taking place at successively higher temperatures at any given pressure. At the temperature appropriate to each step a certain phase assemblage becomes unstable, and each step is characterized by the disappearance of its appropriate phase assemblage. The survival of that phase assemblage in a rock is rigorously indicative of the fact that the step in question has not been attained. In ten of the steps, the disappearance of the phase assemblage is accompanied by a more conspicuous phenomenon, viz., the appearance of a new phase, a metamorphic mineral; this appearance of a new phase, however, cannot be regarded as rigorously indicative of the accomplishment of the step, since the new phase can be produced otherwise. Nevertheless, if certain additional conditions are fulfilled, the new phase will appear only when the temperature of the appropriate step is attained, and the metamorphic minerals then become indicators of grade of metamorphism. In the order of the rising temperature steps at which they are produced, the ten minerals are tremolite, forsterite, diopside, periclase, wollastonite, monticellite, akermanite, spurrite, merwinite, and larnite. Examination of their natural occurrence suggests that they are for the most part produced under conditions which permit their use as temperature indicators.
A.C.B.

Properties of kaolinite as a function of its particle size. C. G. HARMAN AND FELIX FRAULINI. *Jour. Amer. Ceram. Soc.*, **23** [9] 252–59 (1940).

Reaction of calcined phosphate rock with alkali carbonate solutions. KENNETH A. KOBE, WILLIAM S. HAMM, AND ALEXANDER LEIPPER. *Ind. Eng. Chem.*, **32** [7] 981–83 (1940).—A defluorinated phosphate rock was treated with solutions of alkali carbonates, and the extent of transposition of the P_2O_5 was determined when the steady state was attained. The amount transposed increased with both concentration and amount of excess carbonate, amounting to 84% with four equivalents of both sodium and ammonium carbonate. This corresponds closely to the citrate-soluble P_2O_5 in the rock. Conversion decreases with increased temperature. The rate of conversion is influenced by the method of agitation (grinding or shaking). The mechanism of reaction appears to be different for sodium and ammonium carbonates. Methods of separating the trisodium and triammonium phosphates from the solution are discussed. Illustrated.
F.G.H.

Refining of German clays. A. W. SCHMIDT, L. STUCKERT, AND H. BECK. *Sprechsaal*, **73** [21] 183–85; [22] 194–97; [23] 203–205 (1940).—The possibility was investigated of obtaining an artificial bauxite (for use in fine ceramics, the production of alumina, etc.) from a German clay of average composition by adding alkaline alumina. A method for converting the alkali silicate solution, which is a by-product in this alkaline process, into a useful ceramic product is given. The clay used as raw material is calcined to liberate the water of crystallization; this increases the activity of the remaining oxides of aluminum and silicon toward chemical agents. A considerable part of the silicic acid is extracted by heating this residue with a solution of caustic soda. A material with low SiO_2 content and higher Al_2O_3 content remains which is similar in composition to bauxite used in the production of Al_2O_3. In this alkaline extraction, small quantities of Al_2O_3 go into the extraction solution below 1000°; sodium is also retained in the residue. The results of the experiments on a small scale were confirmed by experiments with larger apparatus; the alkaline extraction proceeded in the same manner in larger quantities. The solution used for the alkaline extraction, which contains the alkali silicate and small quantities of alkali aluminate, is converted by heating with caustic magnesium oxide into solid magnesium silicate with a composition regulable within certain limits, and the sodium solution is left. This white Mg silicate contains either free MgO or an excess of free SiO_2 and small quantities of Al_2O_3 and can be used as a raw material for the ceramic industry. Ceramic masses of different composition are made from this Mg silicate mix; they are shaped by hand by casting in molds or by pressing in steel matrices and are fired in ceramic kilns. A porous or a dense magnesium porcelain of a more or less white color is obtained. It is possible to add the Mg silicate mix to ceramic masses which formerly were made with natural Mg silicate masses such as talc (steatite), serpentine, olivene, cordierite, etc. Since the conversion of the alkali silicate solution into Mg silicate forms sodium hydroxide again, the process of extracting the clay becomes a cycle, where only clay and magnesium oxide are added; in the first stage, artificial bauxite is formed, and in the second stage, artificial steatite. Since it is possible to change arbitrarily the composition of Mg silicate mixes so that they can be used at higher sintering temperatures, they can be used in the manufacture of refractory block and furnace linings which are similar to ordinary sintered magnesia products. The superiority of products made in this way over those made with natural raw materials in Germany lies in the fact that indigenous clays can be used in place of imported bauxite and the alumina obtained has the same degree of purity. The Mg silicate as a ceramic raw material is purer than the natural raw material.
M.V.C.

Significance of Montana's mineral industry. FRANCIS A. THOMSON. *Mining Congr. Jour.*, **26** [6] 10–13 (1940).—The total value of the mineral production for all time is $3,300,000,000, of which clay products amounted to $15,-000,000 and miscellaneous, $70,000,000. The miscellaneous includes six minor metals, arsenious oxide, asbestos, cement, corundum, flint, graphite, gypsum, quartz, and six others.
W.D.F.

Specific gravities of clays. V. L. BOSAZZA. *S. African Jour. Sci.*, **34**, 155–57.—Methods and results of the determination of the specific gravity of clays are given. Different liquids were used for the same specimen, and in many cases variable results were obtained. For white residual clays, i.e., kaolins, consistently high values were found, which could not be explained. The amount and the

character of the accessory minerals were known for each specimen. A considerable amount of research remains to be done. The values for the clay minerals are, in general, unreliable. V.L.B.

PATENT

Brucite separation. M. F. GOUDGE. Can. 388,635, May 14, 1940 (March 28, 1939).—The process comprises the production of granular brucite by calcining brucite-bearing limestone, hydrating the calcined product, and separating the resultant granules from the hydrated lime thereby produced. G.M.H.

Chemistry and Physics

Analysis of high-alumina clays by the thermal method. F. H. NORTON. *Jour. Amer. Ceram. Soc.*, **23** [9] 281–82 (1940); see *ibid.*, **22** [2] 54–63 (1939).

Analysis of silicate and carbonate rocks as building materials. V. RODT. *Tonind.-Ztg.*, **63** [42–43] 487–88 (1939).—R. gives practical hints on the determination of silica, alumina, iron, and lime in natural stone. W.K.

Calculation of particle sizes in stratified alumina hydrosols. M. A. MILLER. *Jour. Phys. Chem.*, **43**, 631 (1939).—The rates of stratification of apparently stable alumina hydrosol systems were studied, and calculations of particle size giving results of the right order of magnitude were obtained by applying Stokes' law either alone or in combination with Einstein's equation for Brownian movement. Methods of calculating the amounts of material present and the size distribution of the particles in the stratified zones are indicated. R.A.G.

Colorimetric determination of cobalt with beta-nitroso-alpha-naphthol. JOHN H. YOE AND CHARLES J. BARTON. *Ind. Eng. Chem., Anal. Ed.*, **12** [7] 405–409 (1940).—In a spectrophotometric study of the colorimetric determination of cobalt with β-nitroso-α-naphthol, the optimum conditions for measurements, the effect of salts, and the interference of certain metallic ions were determined. The principal advantages of the method are its high sensitivity and reproducibility. The chief disadvantages are the great influence of the ammonia concentration and the low solubility of cobalt-nitrosonaphtholate. Illustrated. F.G.H.

Correcting ignited silica precipitates for nonvolatile material. JOHN S. BILLHEIMER, PAUL H. FAUST, AND ERNEST H. SWIFT. *Ind. Eng. Chem., Anal. Ed.*, **12** [7] 409–11 (1940).—An experimental study was made of various methods for determining the "nonvolatile residue" in ignited silica precipitates by volatilizing the silica with hydrofluoric acid. For all except the most accurate work a treatment with perchloric and oxalic acids may be substituted to advantage for the sulfuric acid commonly used. Experiments with organic acids of high boiling point have not shown them to possess any marked advantages. F.G.H.

Determination of sodium in the presence of other metals. E. C. ELLIOTT. *Ind. Eng. Chem., Anal. Ed.*, **12** [7] 416–17 (1940).—The magnesium uranyl acetate method for determining small amounts of sodium can be successfully used in the presence of beryllium, cerium, lanthanum, neodymium, thallium, thorium, vanadium, and zirconium. Silica, if present, can be removed with hydrofluoric acid and sulfuric acid. Columbium and tantalum will precipitate in the acid reagent, but no difficulty is encountered if these elements are removed previous to the sodium determination. F.G.H.

Dropping mercury electrode for lead analysis. E. C. BARNES. *Ind. Med.*, **9**, 334 (July, 1940).—B. reports briefly on the apparatus and procedure for determining lead quantitatively in solutions containing only lead and in those containing other ions in addition to lead, such as zinc, cadmium, tin, etc. K.R.

English engineering units and their dimensions. E. W. COMINGS. *Ind. Eng. Chem.*, **32** [7] 984–87 (1940).—A system of units based on force pounds, mass pounds, feet, and seconds requires the occasional use of the dimensional constant β which has the same numerical value as the standard acceleration of gravity, 32.1740, but the units mass pounds × feet/force pounds × second, which are not those of acceleration. The use of this dimensional constant is discussed, and examples are worked out. A clear distinction between force pounds and mass pounds is made. The application of dimensional analysis to problems in fluid motion, involving quantities evaluated in a four-dimension system, yields results which are also applicable to three-dimension systems, and a procedure is illustrated whereby the dimensional conversion factor ($\beta = Ma/F$) is automatically retained in the final result wherever needed. F.G.H.

Extraction of alkalis in rocks. Modification of the J. Lawrence Smith extraction, using barium chloride as a flux. ROLLINS E. STEVENS. *Ind. Eng. Chem., Anal. Ed.*, **12** [7] 413–15 (1940).—S. describes a modification of the J. Lawrence Smith method for the extraction of alkalis from rocks and silicate minerals in which barium chloride is substituted for the ammonium chloride customarily used in the sintering mixture. The two methods are of equal value in completeness of alkali extraction, but the modification allows a saving of time and automatically removes any sulfate the sample contains. The barium chloride method is advantageously used in analyzing alunites because a molten mass does not result and the cake is easily removed from the crucible and disintegrated in water. Neither method seems to be affected by a large magnesium content in the sample. F.G.H.

New group separation for the analysis of phosphates. G. J. AUSTIN. *Analyst*, **65** [771] 335–47 (1940).—The difficulties encountered in the analysis of materials containing phosphates, especially when the amount of phosphorus is in excess of the iron and alumina content, may be solved by a new group separation whereby the phosphorus is utilized in the analysis. The method consists of the following procedures: (1) groups 1 and 2 are removed as usual; (2) Ba and Si are precipitated as sulfates from a 25-ml. solution of approximately $N/5$ HCl; (3) Fe, Al, and Cr are precipitated as phosphates at pH 3.2 to 3.4; (4) Zn, Ni, and Co sulfides are precipitated in a solution buffered to pH 4.6 to 4.8 and treated with H_2S at 70° to 80°C.; (5) after the H_2S is boiled off, Mn is precipitated as the dioxide with sodium hypochlorite; (6) Ca is precipitated as the oxalate; and (7) Mg is precipitated as the phosphate in the usual manner. This procedure may be used for either qualitative or quantitative separations and determinations. B.C.R.

Properties of mixtures of air and saturated water vapor for barometric pressures from 22 to 32 in. of mercury. WILLIAM GOODMAN. *Heating, Piping & Air Conditioning*, **12** [7] 435–36 (1940).—The tabulation of values for 32 in. of mercury completes this series of tables. See *Ceram. Abs.*, **19** [9] 220 (1940). J.L.G.

Quantitative separation of metals by hydrogen sulfide: III, Quantitative separation of zinc from iron by hydrogen sulfide and the induced precipitation of ferrous sulfide by zinc sulfide. HISAJI KATO. *Science Repts. Tôhoku Imp. Univ., Series 1*, **28**, 480–90 (1940); for Parts I and II see *Ceram. Abs.*, **17** [11] 366 (1938). W.D.F.

Quantitative spectrographic analysis: I, Method of relative intensities with internal standard. J. T. MIRELES MALPICA. *Gen. Elec. Rev.*, **43** [7] 288–97 (1940).—The advantages and application of spectrochemical analysis are discussed. Three methods of excitation of the emission spectra exist: flame, arc, and spark. The process involved and the electrical and optical apparatus are described, together with an experimental investigation of the obvious sources as a preliminary step in analytical operations. L.E.T.

Rate of decomposition of kyanite at various temperatures. HELEN BLAIR BARLETT. *Jour. Amer. Ceram. Soc.*, **23** [9] 249–51 (1940).

Relationships between composition of slags and their role in steel manufacture. T. NÉGRESCO AND W. J. CROOK. *Bull. Acad. Sci. Roumaine*, **18**, 74–80 (1936–37); *Brit. Chem. & Phys. Abs.-B*, **59** [3] 210 (1940).—A further discussion is given of the quaternary diagram of the system $SiO_2 + FeO + Fe_2O_3 + (CaO + MgO)$ and of the constitution of steel slags. See "Constitution...," *Ceram. Abs.*, **16** [7] 222 (1937).

System alkali oxide–CaO–Al_2O_3–SiO_2–CO_2: VII, Influence of catalyzers on the reaching of the equilibrium between calcite and wollastonite. C. KRÖGER AND K. W. ILLNER. *Z. Anorg. & Allgem. Chem.*, **240** [3] 273–83 (1939).—The influence of the catalyzers CaF_2, NaF, $CaCl_2$, $PtCl_2$, Na_2WO_4, and WO_3 on the calcite-wollastonite equilibrium was investigated. All of these compounds affect the reaction only through their small, but always present, water content with the exception of $PtCl_2$, which above 600°C. apparently influences the inversion of the quartz. The presence of water effects the formation of crystals of calcium metasilicate; otherwise, the orthosilicate is formed. The center of crystallization is $CaSiO_3 \cdot xH_2O$. X-ray spectrograms, however, show only secondary lines of $CaSiO_3$. For Part VI see *Ceram. Abs.*, **18** [1] 9 (1939). W.K.

System vanadium–sulfur. W. BILTZ AND A. KÖCHER. *Z. Anorg. & Allgem. Chem.*, **241** [4] 323–37 (1939).—The existence of vanadium monosulfide, sesquisulfide, and tetrasulfide is verified; the existence of the pentasulfide, however, could not be verified. Data from tension analyses and X-ray analyses are presented. R.K.

Two-component systems of germanium: I, Germanium–aluminum, germanium–tin, germanium–silicon. H. STÖHR AND W. KLEMM. *Z. Anorg. & Allgem. Chem.*, **241** [4] 305–23 (1939).—Aluminum and germanium as well as germanium and tin form eutectic systems. The solution in the solid state was determined by means of X rays. Germanium and silicon form an unbroken series of mixed crystals. The attainment of equilibrium in the solid state is unusually slow. The lattice constants in the mixed crystals are approximately additive. The behavior of aluminum is compared with that of the elements of the fourth group which is also discussed. The solution in the solid state is strongly reduced when the two elements show real differences in metallic characteristics. R.K.

BOOK

Water Glass, Its Characteristics, Production, and Application (Das Wasserglas, seine Eigenschaften, seine Herstellung, und Verwendung). HERMANN MAYER. Fried. Vieweg & Sohn, Braunschweig, 1939. 2d enlarged ed. 123 pp., 21 illustrations. Price 7.20 Rm. Reviewed in *Chem.-Ztg.*, **63** [56] 494 (1939).—M. gives all known information up to the present time concerning water glass. Of particular importance is the section of the book devoted to the application of water glass. D.A.B.

PATENTS

Apparatus for producing alkali silicates. P. W. SODERBERG (J. B. Ford Co.). U. S. 2,211,734, Aug. 13, 1940 (March 18, 1938; June 11, 1938).

Manufacture of alkali metals by electrolysis. E. I. DU PONT DE NEMOURS & CO. AND R. E. HULSE. Brit. 522,635, July 3, 1940 (Dec. 15, 1938).

Producing alkali silicates. P. W. SODERBERG (J. B. Ford Co.). U. S. 2,211,733, Aug. 13, 1940 (March 18, 1938).—The process of producing a granular form of an alkali-metal silicate comprises mixing silica with not less than the same amount of caustic alkali, advancing the mixture in a continuously moving stream, subjecting the mixture during its advancement to a mixing operation and to heat, regulating the rate of advancement of the stream and the temperature of the heat applied so that the active chemical reaction of the mixture occurs in an intermediate section of the length of the moving stream, enclosing sections of the stream on opposite sides of the intermediate section to thereby protect the sections of the stream from direct contact with the atmosphere, venting to atmosphere the intermediate section of the stream in which the active chemical reaction takes place in order to exhaust the water vapor arising therefrom, and causing some moisture to be retained in the stream after it leaves the intermediate vented section to provide moisture in the final product.

Production of double fluorides of alkali metals and aluminum. H. W. HEISER. Brit. 522,987, July 17, 1940 (July 29, 1938).

Recovering magnesium oxide. H. R. BRANDENBURG. U. S. 2,210,892, Aug. 13, 1940 (Feb. 9, 1938).—The method of obtaining free or available magnesium oxide from serpentine consists in calcining the serpentine at a temperature between 500° and 900°C. to liberate the magnesium oxide, suspending the calcine in water while passing carbon dioxide gas through the suspension for forming bicarbonate of magnesium in solution, filtering to separate the bicarbonate of magnesium solution from the residue, evaporating the filtrate thus obtained to precipitate magnesium carbonate, filtering to separate the thus precipitated magnesium carbonate, and heating the magnesium carbonate to obtain magnesium oxide.

General

Ceramic extension program of the Pennsylvania State College. EDWARD P. MCNAMARA. *Bull. Amer. Ceram. Soc.*, **19** [8] 318–21 (1940).

Determination of the size of particles of dusts. A. WINKEL. *Chem. App.*, **26** [17] 265–69; [18] 281–83 (1939).—The importance of knowing the fineness of dust is discussed. The fineness determines the setting time of cements, the reduction velocity of Zn dust, the covering power of pigments, etc. The methods by which fineness is determined, either directly or indirectly, and the instruments used are surveyed. Each method and the formulas necessary for evaluating the measurements are described. Thirty references. M.H.

Dust control in rock drilling. LEONARD GREENBURG, T. F. HATCH, W. J. BURKE, AND W. B. HARRIS. *Amer. Jour. Pub. Health*, **30** [5] 463–76 (1940).—In the New York State code on rock drilling, the maximum allowable dust concentration for materials containing less than 10% free silica is 100 million particles per cu. ft., and that for rocks containing over 10% free silica or having a variable or an unpredictable free-silica content is 10 million particles per cu. ft. Knopf's method is used for determining the free-silica content, which is checked roughly by the following method of calculation. By knowing the total silica content and assuming that one half of the silicates is composed of SiO_2, the free-silica content may be calculated roughly after determining (1) the weight of the material insoluble in HCl which is considered to represent the free silica plus the silicates and (2) the residue, i.e., the R_2O_3 associated with the silica as silicates after treatment of the HCl insoluble material with HF and H_2SO_4. Both the determined and calculated values may be subject to considerable error due to the type of the material tested. Wet drilling and different means of providing adequate ventilation are also discussed. ABSTRACTER'S NOTE: A much more satisfactory method for determining free silica is described by L. J. Trostel in *Jour. Amer. Ceram. Soc.*, **22** [2] 46–50 (1939). Of several methods studied, the Knopf procedure was the least and Trostel's the most satisfactory. B.C.R.

Dust elimination and other measures for the prevention of silicosis in the refractory industries. G. BARTHELMESS.

Tonind.-Ztg., **62** [92] 1025–27; [93] 1051–54 (1938).—Free silica is the most frequent cause of silicosis. Silicates are less dangerous, with the exception of asbestos. In addition to allergy, the following factors are important: the kind of dust, its fineness, its density, and the time of exposure. All machines must be tightly covered and the dust must be exhausted. The proper methods are discussed in detail. Other measures include partition walls, work in the open whenever possible, and sweeping and cleaning after working hours. Masks are effective but cannot be worn continuously. The protective installations are expensive. W.K.

Fluorescent lighting. R. G. Slauer. *Factory Management & Maintenance*, **98** [6] 71–74 (1940).—S. warns against (1) expecting a perfect match with daylight, (2) d.-c. operation, (3) use in cold surroundings without proper precautions, (4) use of lamps in the line of vision, (5) fixtures mechanically or electrically unsound, and (6) overrating the efficiency of the lamps in planning a design. Two photographs and one table of lamp sizes, wattages, light output, and list prices. J.L.G.

Health and safety. C. M. Fellman. *Mining & Met.*, **21** [397] 24 (1940).—F. discusses the excellent safety record maintained during 1939 in the various mines and quarries throughout the U. S. J.J.H.

High-calcium therapy. Irving Gray and Irving Greenfield. *Ind. Med.*, **8**, 507–10 (Dec., 1939).—The authors call attention to the danger of the prolonged use of high calcium therapy in the treatment of lead poisoning. In the past 10 years they have observed and treated approximately 250 patients ill with industrial lead poisoning. Active mobilization of lead in the system by the continued use of high calcium dosage, following removal from the occupational hazard, led in several instances to irreversible reactions from the effects of lead upon the peripheral nervous system; four such cases are described in detail. Cases 1 and 2 developed an irreversible bilateral wrist-drop, case 1 also having a drop of the middle finger. Case 3 culminated in a neuritis of the 8th cranial nerve, with resultant deafness and neuritis of the left brachial plexus; case 4, within two weeks, gave evidence of a permanent, progressive, irreversible, peripheral neuritis. The literature (17 references) from 1913 to the present time is reviewed, the experimental and research results being especially drawn upon. From the evidence presented it is ascertained that calcium administered over a long period of time inhibits the deposition of lead in the system and hence is not without therapeutic danger. K.R.

Industrial dermatitis. Committee on Healthful Working Conditions, National Assn. of Manufacturers. *Safety Eng.*, **79**, 35–37 (June, 1940).—Claims for compensation due to skin damage in industrial work reported in incomplete state reports and to the Office of Dermatoses Investigations of the U. S. Public Health Service have constituted about 65% of all reported occupational disease cases. The economic loss to employees and employers is largely preventable. Although the information in this summary is general in character, an effort has been made to treat the subject so that the practical control of a specific dermatitis problem can be set up. The industries most affected by dermatoses are listed in detail. F.S.M.

Inhalation of dust in the chrome brick industry. A. E. Galloway et al. *Ind. Med.*, **9**, 332 (July, 1940).—Microscopic components of the various materials used in making chromium brick include chromite, magnesite, kaolin, refractory cement, and olivine (Mg silicate). The average dust determination showed 371 million particles and an average of 7 1/3% total silica; the average in mixing and molding operations showed 177 million particles with 50% free silica. In the manufacture of chrome brick the workers are exposed to chromite, magnesite (Mg silicate), and silicates; the range of dust concentration is from 800 to 600 million particles per cu. ft. of air, and the range of total silica is 25 to 50 gammas per gm. K.R.

Knudsen prize award. Leroy U. Gardner. *Ind. Med.*, **9**, 351–54 (1940).—The Knudsen prize award, established by William S. Knudsen as an appreciation of the part research has taken in the increased health and efficiency of workers, was awarded for 1939–1940 to Leroy Gardner for research in the control of silicosis which has brought it within the field of preventable occupational diseases. See "Recent developments...," *Ceram. Abs.*, **19** [8] 205 (1940). K.R.

Modifying influences of silicosis and silicosis with infection on the healthy chest. E. P. Pendergrass and P. J. Hodes. *Radiology*, **34**, 400–404 (April, 1940).—Fibrosis of any origin, interfering with the normal massage action of the lung, predisposes to the accumulation of silica and pulmonary fibrosis. If factors favoring further fibrosis, such as additional silica, vascular stasis, or infection are avoided, there is no reason why patients with minimal fibrosis may not remain well. If chronic or acute pulmonary infections supervene, however, little can be done to prevent fibrous overgrowth and progression to massive fibrosis. The hazard should be limited in patients with stabilized lesions, and men with evidence of superimposed active infection should be removed from industry. The latter, if properly guided, may be returned to health even in the face of an active infection. F.S.M.

Ore concentration and milling. E. W. Engelmann. *Mining & Met.*, **21** [397] 36–39 (1940).—E. discusses improvements in grinding, gravity separation, cyanidation, flotation, and dust control during the past year. J.J.H.

Plant testing of ceramic materials with standard pyrometric cones. Arthur J. Blume. Thesis, Ohio State Univ., June, 1940; abstracted in *Ceram. Ind.*, **35** [2] 36–37 (1940).—B. reports a study made to develop a method of checking fusion characteristics of individual nonplastic materials in combination with other nonplastics. Materials were formed into pyrometric cones of the same size and shape as standard small-series cones. A triaxial diagram of the three main nonplastics was set up, and results were interpreted as follows: (*a*) when feldspar and pyrophyllite are varied with flint held constant, 4.5 parts are equal to one P.C.E.; (*b*) when feldspar and flint are varied with pyrophyllite constant, 5.75 parts equal one P.C.E.; (*c*) when flint and pyrophyllite are varied with feldspar constant, 20 parts equal one P.C.E. From these results, B. can take any incoming shipment, make up a small cone batch, fire with standard cones, note deviations, and adjust factory body batches so that the total nonplastic addition will have a P.C.E. equal to the standard. The same method may be used on materials not previously included. Illustrated. L.M.C.

Profits in air—Ford Motor Company. C. Strock. *Heating & Ventilating*, **37** [6] 32–38 (1940).—S. describes an extensive exhaust system for 235 pieces of equipment. One section of the building required the exhausting of grinding machines; the other, where heat-treating and hardening were carried out, necessitated the removal of gases from the numerous furnaces. A remarkable feature of the exhaust system serving the grinding department is the almost total absence of visible duct work. This is achieved by carrying the exhaust connection under the floor to a main located under the aisle and thence to a riser located along the side wall of the building. As the risers are relatively flat and located along the wall, they are practically unnoticed. The method of concealing the branches and main duct under the floor is illustrated. The problem of clean-out doors in the underfloor duct system was nicely solved. On the roof are 15 banks of dust collectors consisting of 92 units capable of handling 92,000 cu. ft. per min., each bank serving an aisle. To maintain a constant static pressure, the filter bags are cleaned automatically by a pneumatic shaking mechanism which agitates the bag. The heat-treating equipment is arranged longitudinally through the hardening room. An enclosure was built in front of all the furnaces extending over their tops in order that they might present a uniform appearance and be heat-insulated from the working space. Each of the furnaces is heavily insulated. Three exhaust systems serve the furnaces and have a combined capacity of 58,100 cu. ft. per min. Gas explosions are eliminated by automatic gas-escape valves. The ducts are also provided with

back-pressure dampers to prevent the fan from discharging back into the building when one is shut down; this also prevents heat loss by stack action. Where the vapors are hot and liable to discolor, an inside casing with air space is provided. This system effectively eliminates any potential hazards without obstructing light or sacrificing appearance. In the author's words, "the exhaust systems in the Ford Tool and Die Shop approach the ultimate in good plant housekeeping." F.S.M.

Recent progress in the nonmetallics. OLIVER BOWLES. *Mining & Met.*, **21** [398] 95–100 (1940).—B. discusses the more important developments in the processes and equipment for and the use of the following nonmetallics or industrial minerals: (1) building materials: aggregates, cement, lime, gypsum, stone, and mineral wool; (2) ceramic raw materials: clay, feldspar, and nepheline syenite; (3) fertilizer materials: potash and phosphate; (4) refractories: pinite and dolomite brick; and (5) other industrial minerals: abrasive materials, asbestos, bentonite, fluorspar, mica, serpentine, sulfur, and topaz. Illustrated. See "Nonmetallic...," *Ceram. Abs.*, **19** [7] 174 (1940). J.J.H.

Lewis P. Reese. E. D. SHUMAKER. *Bull. Amer. Ceram. Soc.*, **19** [8] 302–304 (1940).

Silica hazards in steel-plant practice. D. E. CUMMINGS. *Ind. Med., Ind. Hyg. Sect.*, **9**, 43–44 (July, 1940).—C. comments on silica dust hazards localized in certain interior parts of steel plants. Refractory materials containing considerable proportions of dangerous free silica are widely used in the industry. At the bottom house, materials composed almost entirely of free silica, such as ganister, sand rock, river sand, and broken silica brick, are ground dry in large mullers with the production of high dust concentrations. At the open hearth and elsewhere in the plant, many varieties of dusty silica-containing brick are unloaded by hand from railroad cars and stored in sheds prior to their use for building or repairing furnaces or for lining ladles. Finely ground dry ganister, fire clay, and silica sand, alone and in combination, are unloaded by crane from open gondola cars and are stored in bins for the preparation of refractory cements or mortars. Laborers tear down highly siliceous open-hearth furnaces and checker chambers with dry pneumatic drills; masons rebuild them with dry and dusty silica-containing brick. Both laborers and masons are alike exposed to silica dust in cleaning, repairing, or reconstructing blast furnaces, linings of blast furnaces, the refractory portion of power-plant boilers, or furnaces and soaking pits in a rolling mill. Kammer found that more than one fourth of a group of steel-plant masons were silicotics. The steel-plant foundry also offers exposure to silica dust during such operations as sand preparation, shakeout, chipping, and the cleaning of castings. Annealing at the sheet mill is accompanied by silica dust evolved from the sand used to seal the trays in which the steel is housed. Men operating cranes in any department which utilizes or processes silica-containing materials are also exposed to a hazard from the fine dust carried to them by the ascending air. K.R.

Silicotuberculosis in a large industrial center. B. H. DOUGLAS AND E. TOMPKINS. *Radiology*, **34**, 405–10 (April, 1940).—One hundred thirty-two cases of silicotuberculosis were admitted to the hospital. Their occupations varied, the largest number, 73, having been foundry workers. The failure of collapse therapy as a measure to be employed for silicotuberculosis is pointed out. The serious prognosis is stressed, and the need for an accurate diagnosis is emphasized in the interest of proper treatment. F.S.M.

Use of stone dust in controlling coal-dust explosions from the hygienic standpoint. HAYO BRUNS, W. CEELEN, AND O. EHRISMANN. *Arch. Gewerbepath. & Gewerbehyg.*, **9**, 509–58 (1939).—Various theories accounting for explosions in coal mines during the 19th century are reviewed. Gases released from the coal, fugitive sparks, and inflammable dusts developing in mining operations were elements of the problem. Research for explosion causes was carried on for at least 80 years in coal-mining countries, but explosions continued to occur. In northern France in 1906, 1100 miners were sacrificed; by 1910, ten other great explosions had occurred, largely in North America, with a loss of 1000 miners. Laboratory experiments bringing about artificial explosions were instituted and carefully studied. Before and after the World War the campaign for explosion control was reinforced by the systematic spraying of mine interiors with noncombustible dusts such as slate clays, caldron ashes, and similar inert substances. Bruns and Ceelen were among the earlier investigators of the new method, Ehrismann joining them in 1933. By 1926, German mining police regulations had incorporated many of the research results as mandatory; 9 specifications are listed. Reassuring reports of the new procedures began to be modified by alleged serious effects upon coal miners from constant inhalation of the sprayed and scattered dusts. Miners protected from explosions might eventually fall victims to silicosis. Alkaline components of the protective dusts were thought to weaken their harmful action on lung tissues; hence, in the porcelain industry, special precautions had to be taken against silicosis, as porcelain and pottery clays had no alkaline components. Facts and theories relative to the origin of the dust diseases at present utilized for their prevention are reviewed by the authors as a preliminary to their own contribution, based upon their detailed and comprehensive study of stone dusts used in the Ruhr area for the period 1923 to 1936; 562 tests were applied to 63 kinds of dusts and dust combinations used in coal mines for mine spraying, the samples being derived directly from the mines themselves or commercially provided. The procedure in testing the samples is given in detail; it involved experiments on 200 rabbits and 1000 guinea pigs. Microscopic sections from the lungs of pit horses who had lived 12 or 13 years underground in mining atmospheres were also studied, but they yielded no evidence of characteristic changes from prolonged dust exposures. Apparatus used in the stone-dust tests and animal experiments is illustrated, together with microscopic sections of the commonly used stone dusts and 7 slides of the lungs of guinea pigs after exposure to the same stone dusts. Results of these researches represent 15 years of explosion control by protective dusts in mines employing 300,000 coal miners actively working during this period. No case of silicotic invasion of lung tissue could be directly traced to the inhalation of the stone dusts. Seven individual reports are submitted in the form required by the Boards of Compensation for occupational injuries; tests, procedure, and comment upon the stone dusts involved, such as slate clays, calcium, and those obtained from private firms, are presented in full. K.R.

Venturi ejector for handling air: I, Experimental study of the ejector. F. F. KRAVATH. *Heating & Ventilating*, **37** [6] 17–21 (1940).—In an effort to answer questions which might be raised by an engineer, K. conducted a series of experiments on what is considered the most efficiently shaped Venturi ejector. The results indicate that the induced air volume is virtually a straight-line function of the jet volume. Resistance applied on the induction side of the ejector resulted in an expected decrease in induced air volume. Under identical conditions, a 2-in. jet induces 600% of the air of a 6-in. jet and 250% of the volume of a 4-in. jet. As the induction resistance is increased, however, the relative superiority of the smaller jets decreases somewhat, but at free delivery it is possible to induce an air volume approximately $5^1/_2$ times the volume of the jet air. K. emphasizes the reduction of resistance at the ejector discharge to an absolute minimum. Even a small amount of additional resistance, such as would only decrease the induced air 25 to 40% if applied at the induction or secondary end, is enough to destroy completely the effectiveness of the ejector if applied at the discharge end. Not only is no air induced, but some of the jet or primary air actually reverses direction and comes out the secondary end. This can be avoided by making any length of pipe as large in diameter as is practicable; elbows should be of the long radius, multipiece type, and weather caps should be streamlined to avoid unnecessary

shock losses. If resistance cannot be avoided, the jet velocity must be increased. F.S.M.

Working hours in the heavy-clay industry. ANON. *Refrac. Jour.*, **15** [8] 353 (1939).—British laws pertaining to the employment of persons under 16 years of age in the heavy-clay industry are discussed. B.C.R.

SEPARATE PUBLICATION

Molten lead, lead oxides, white lead, and lead dry-colors. F. W. ECKFELDT. *Penna. Dept. Labor & Ind., Safe Practice Bull.*, No. 19 (Feb., 1940). 10 pp., 11 illustrations. F.S.M.

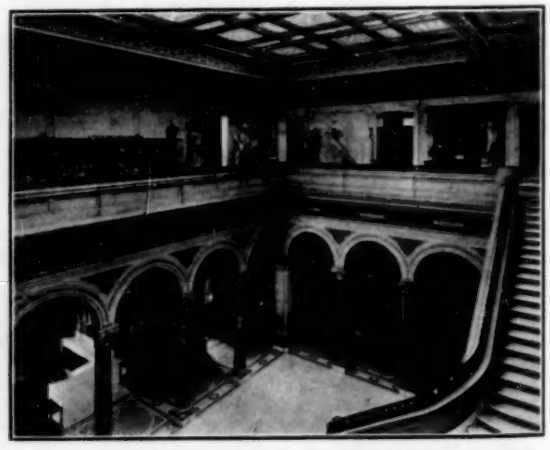
FORTY-THIRD ANNUAL MEETING OF THE AMERICAN CERAMIC SOCIETY

BALTIMORE, MARYLAND, MARCH 30 to APRIL 5, 1941

Walters Art Gallery Exterior View

Chinese Porcelain Exhibit in Walters Art Gallery

Maryland Institute Exterior View



Maryland Institute Interior View

OFFICIAL PERSONNEL OF DIVISIONS, 1940–1941

	Art	Enamel	Glass	Materials and Equipment	Refractories	Structural Clay Products	White Wares
Trustee	L. E. Barringer	J. E. Hansen	D. E. Sharp	H. B. DuBois	J. D. Sullivan	A. F. Greaves-Walker	E. H. Fritz
Chairman	H. S. Nash	J. D. Tetrick	W. R. Lester	B. T. Bonnot	J. B. Austin	H. Z. Schofield	Harry Thiemecke
Vice-Chairman	K. E. Smith		A. K. Lyle	W. H. Emerson	Gilbert Soler	J. H. Isenhour	
2nd Vice-Chairman			W. C. Taylor				
Secretary	C. C. Engle	D. G. Bennett	S. R. Scholes	S. S. Cole	R. S. Bradley	L. R. Whitaker	R. Russell, Jr.
Society Nominations A.....	M. M. French	B. T. Sweely	F. C. Flint	W. R. Malkin	G. A. Bole	R. L. Stone	L. E. Thiess
Society Nominations B.....	C. C. Engle	R. R. Danielson	W. M. Clark	H. R. Straight	S. M. Phelps	T. W. Garve	D. C. Zimmer
Division Nominations	Ruth Canfield A. A. Ayars	H. G. Wolfram	A. N. Finn				
Papers and Program	W. A. Weldon Carlton Atherton J. P. Thorley	R. L. Fellows	A. K. Lyle W. C. Taylor	S. S. Cole J. R. Kauffman R. Buchholz	C. L. Thompson W. R. McLain G. S. Diamond W. R. Kerr	H. D. Foster F. E. Lobaugh J. E. Rankin	F. C. Henderson Howard Failmezger C. G. Harman
Membership	H. E. Marley H. H. Sanders	Karl Kautz	C. B. Delgado	J. T. Robson	C. A. Freeman	J. H. Stewart	G. J. Bair
Standards	A. E. Baggs	F. W. C. Hutchison	G. W. Morey	W. H. Vaughan	P. S. Dear	H. C. Plummer	J. H. Koenig
Research	H. F. Bopp	R. J. Whitesell	N. W. Taylor	J. F. McMahon	D. W. Ross	Frederick Heath, Jr.	J. R. Beam
Data	Marion Fosdick P. E. Cox	P. C. McCollom	A. E. Badger	R. G. O'Meara	P. G. Herold	H. G. Schurecht	G. A. Loomis
Rules	Theodore Lenchner	G. H. Spencer-Strong	A. N. Finn	J. E. Eagle	R. B. Sosman	G. H. Duncombe, Jr.	K. E. Stettinius
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